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投稿規定

1　資　格

原則として，気象庁職員に限る。ただし，気象庁職員との連名の場合は，この限りでない。

2　論文及び報文（以下「論文等」という。）の内容

未発表の原稿で，海洋（物理・化学・生物・地質など）及び海上気象（波浪・海氷・海気相互関係など）に関する論文並びに気象庁における海洋・海上気象業務の活動，そのために開発された測器及び方法に関する報文など。

3　書き方

(1)　用語は，欧文（原則として英文）とする。

(2)　論文等には，英文（300語以内）及び和文（800字以内）の要約を付ける。要約は，方法・測器・実験・観測の結果・仮定・理論などの中味が読みとれるように留意し，なるべく指定の長さで簡潔に書く。

(3)　論文等の始めには，題名・著者名及所属機関名を明記する。和文の要約にも同様のことを明記する。

(4)　原稿は，厚手の用紙にダブルスペースでタイプする。

(5)　図は，白紙又は青方眼紙に墨入れし，図及び図中の文字の大きさは，印刷の際の縮小率を考えて作成する。特に重要な図は，投稿者が大きさを指定する（印刷の都合上，希望どおりにならないこともある。）

(6)　図（写真を含む。）及び表には，必ず説明を付ける。図の説明文は，別紙にタイプする。折り込みの図及び表は，なるべく避ける。図及び表のそう入箇所を本文の欄外に記入する。

(7)　数式は，2行取りに書き，数式の文字及び記号をはっきりと説明する。

(8)　論文等の中に文献を引用する場合は，「ALLEN (1927)」又は「(ALLEN, 1927)」のように書く。

(9)　引用文献は，最後にまとめて付け，著者名のアルファベット順に並べる。書き方は次のようにする。

ALLEN, W.E. (1927): Surface catches of marine diatoms and dinoflagellates made by U.S.A. Pioneer in Alaskan waters in 1923. *Bull. Scripps Inst. Occanogr., Tech. Ser.* **1**(4), 39–48.

BUDYKO, M. I. (1956): *The heat balance of the earth's surface.* Hydrometeorogical Publishing House, Leningrad, pp. 254.

VERONINS, G. and H. STOMMEL (1956): The action of a variable wind stress on a stratified ocean. *J. Mar. Res.*, **15**(1), 43–75.

4　提出方法

投稿票を付け，本稿のほかにコピー（図及び表を含む。）2部を添える。

5　締切り

毎年気象庁公報により公示する。

6　送付先

気象庁海洋気象部海洋課

（原則として，書留便で送付する。）

7　その他

論文等1編につき別刷り50部を著者に無料で送付する。

Oceanographical Magazine

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Biogeochemical behavior of nitrate and phosphate in the ocean

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Abstract: It was clarified that concentrations of nitrate and phosphate in sea water can be expressed as a sum of a constant term (primary concentration) and a variable term (plus or minus). In the upper layer from surface to 1 km, variation in concentration is caused mainly by organic production, while in deeper layer, by decomposition of organic matters. The primary concentration is defined as concentration when biological production and AOU are zero.

Results of calculation using observed values of nitrate ion concentration (N) and AOU at 54 stations locating from 65°S to 17°N along 100°W and 146°W in the Pacific showed that relation between nitrate ion concentration and AOU is linear and the ratio of their rates of change is 0.043 and the primary concentration is 20.2 μg atoms liter^{-1}. Using these values nitrate ion concentration is calculated below 1 km depth in wide areas of the Pacific. Results agree well with observations.

For phosphorus ratio between rates of change of phosphate ion concentration (P) and AOU is 0.0029 and the primary concentration is 1.58 μg atoms liter^{-1}. The phosphate ion concentration is calculated in the deeper layer of which results coincide very well with observations. It is theoretically made clear that N/P ratio in sea water is determined by difference between primary N/P ratio (12.8) and $\Delta N/\Delta P$ ratio (15). N/P ratio near the surface is lower than 12.8 due to biological production, and higher in the deep up to 14. Results of calculation of N/P ratio from surface to bottom at different stations show a good agreement with observation.

1. Introduction

Nitrogen and phosphorus are important and indispensable nutrients for marine organisms in spite of their small concentration in sea water. Both of these elements in the ocean are repeating the continuous and incessant cycle from inorganic to organic and vice versa through biological production and oxidative decomposition of organic matter. Therefore, dissolved nitrogen and phosphorus in sea water are present not only in inorganic forms (mostly nitrate and phosphate ion) but also in various kinds of organic compounds which are produced in the course of decomposition of proteinous matter.

Up to the present, however, owing to the lack of facile methods of chemical analysis, it is rather difficult to obtain reliable data on the content of organic compounds of

nitrogen and phosphorus in sea water. On the contrary, a large number of analytical data on the contents of nitrate and phosphate ions* in sea water is accumulated.

According to the results of observations, concentrations of both ions are lower near the surface of the ocean, and they increase with increasing depths to about 40 μg atoms liter^{-1} and 3μg atoms liter^{-1} respectively for nitrate and phosphate. As to the horizontal distribution, it is found that the surface concentration of these ions are extremely low (down to zero) in the subtropical regions, and they increase toward the higher latitude on both hemispheres (up to about 20μg atoms liter^{-1} and 2μg atoms liter^{-1} respectively for nitrate and phosphate). It is known also that nitrate and phosphate are enriched in surface sea water in the upwelling zones, for example, in the sea area along the Peruvian Current in the tropical Pacific.

The reason for the wide variation in nitrate and phosphate concentrations in sea water is the change in the rates of biological and biochemical processes which differ considerably with location and depth. In addition the movement of sea water on the horizontal and vertical directions is another important cause which brings about the variation in nitrate and phosphate concentrations in sea water.

In order to clarify the variation of nitrate and phosphate concentration in sea water in different sea areas, REDFIELD, KETCHUM and RICHARDS (1963) studied on the relation between the concentration of nitrate or phosphate and the apparent oxygen utilization (AOU), and they proposed a new concept of the preformed nitrate or phosphate concentration (at AOU=0) observed near the sea surface which differ considerably from area to area.

In this report, using observed values of nitrate and phosphate contents in sea water in wide areas of the Pacific, the biological and biochemical processes of these elements are discussed by applying the same manner with which two of the present authors (MIYAKE and SARUHASHI, 1976) previously studied on the carbon system in the ocean. As the result, it was found that the nitrate and phosphate concentrations when there is no oxidation reaction and no biological production in sea water are nearly constant in the ocean.

2. On nitrate in sea water

According to the results of observation, the concentration of nitrate near the surface of the ocean is lower owing to the loss due to biological production. On the contrary, the concentration of organic nitrogen must be higher near the surface. In the deep layer, the concentration of nitrate increases due to the oxidative decomposition of organic debris and, in reverse, the concentration of organic nitrogen must decrease.

The concentration of nitrate in sea water may consist of two terms, one is constant and another is variable as follows.

---

* For the sake of simplicity nitrate ion and phosphate ion are called as nitrate and phosphate in the text.

$$N = N_0 + \Delta N \ (\mu g \text{ atoms liter}^{-1}) \qquad (1)$$

where N, N_0 and ΔN denote respectively the concentration of nitrate, the primary concentration of nitrate and their difference. As to the meaning of N_0, explanations will be given later in detail.

Several years ago two of the present authors (MIYAKE and SARUHASHI, 1976) discussed the biogeochemical cycle of carbon in the ocean. Applying the same manner, the biogeochemical cycle of nitrogen in the ocean is investigated.

In considering the geochemical cycle, the ocean is divided simply into two layers, i.e., one is called the first layer (0–1 km) and another the second layer (1–4 km).

The variation in the concentration of nitrate (N μg atoms liter^{-1}) in sea water in the first layer can be expressed as follows.

$$\Delta N = \alpha AOU - \Delta N_b - \Delta N_d \qquad (2)$$

where αAOU is the concentration of nitrate which is reproduced through oxidative decomposition of organic nitrogen. AOU is the apparent oxygen utilization in μg atoms liter^{-1} and α is a constant factor (<1.0) relating to AOU. ΔN_b is a concentration of nitrate which is converted to organic nitrogen through biological production. ΔN_d is a concentration of nitrate which is reduced to gaseous nitrogen (N_2) through denitrification. As denitrification takes place only in limited areas of the ocean in which anarobic conditions are observed, it is assumed here that ΔN_d is negligible.

In the second layer of the ocean, N can be expressed simply as follows since there is no biological production.

$$N = N_0 + \alpha AOU \qquad (3)$$

when α is known, N_0 can be estimated by using observed values of N and AOU in the same water sample. Then, using the calculated value of N_0, the value of ΔN_b in the Eq. 2 can be deduced.

(1) On the factor α relating to AOU

α is a fraction of AOU (μg atoms liter^{-1}) which plays a role in oxidizing organic nitrogen to nitrate.

In 1971, one of the present authors (SAGI, 1977) made an extensive study on N and AOU in sea water collected at 54 stations along meridional lines of 100°W and 146°W extending from 65°S to 17°N in the Pacific, during the cruise (KH 71-5) aboard the R.V. Hakuho-maru which belongs to the Ocean Research Institute of the University of Tokyo. The tracks of the cruise are shown in Fig. 1.

Using the data on N and AOU obtained during the above expedition, the evaluation of α was done. In order to derive a value of α, the mean values of N and AOU in sea water in three successive layers on every station, i.e., the layers from 1 to 2 km, 2 to 3 km and 3 to 4 km depth at the above 54 stations were calculated.

A result of plotting the values of N versus AOU is shown in Fig. 2. As shown in Fig. 2, there is a linear relation between N and AOU which can be expressed by the next empirical equation (unit, μg atoms liter^{-1}).

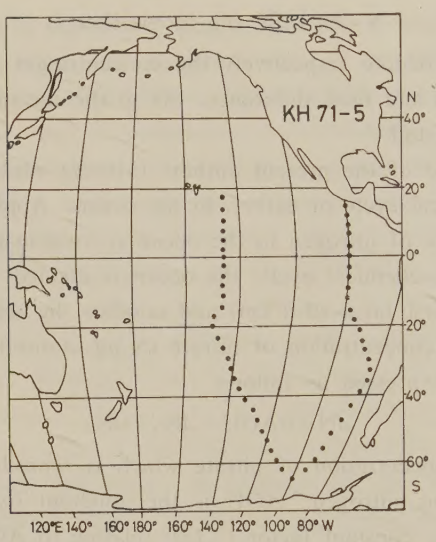

Fig. 1. Hydrographic stations of cruise KH 71-5 (1971) of Hakuho Maru (Ocean Research Institute, University of Tokyo).

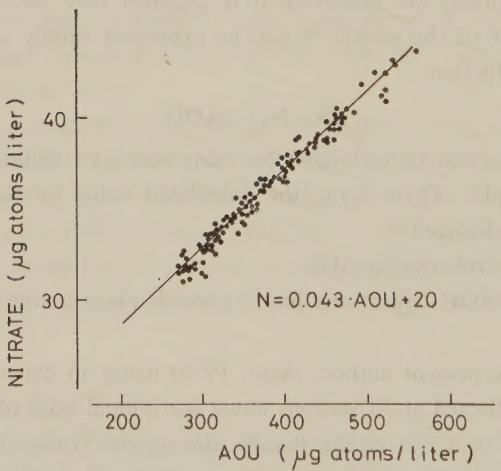

Fig. 2. Relation between nitrate concentration and AOU.

$$N = 0.043\,AOU + 20$$

in which the value of α of 0.043 is determined by least square between N and AOU. A constant of about 20 (μg atoms liter^{-1}) corresponds to the primary concentration of nitrate on which further discussion will be given in the next section.

As well known, in the oxidation reaction of organic nitrogen to nitrate, four oxygen atoms are needed for one atom of nitrogen. Therefore, in this reaction, 0.043×4 or

17.2% of AOU is consumed in total in which 0.043×3 or 12.9% is used for the formation of one NO_3^- ion.

(2) On the primary concentration of nitrate, N_0

In the above section, the value of N_0 of 20μg atoms liter^{-1} was obtained graphically. In this section a further discussion on the implication of N_0, the primary concentration of nitrate is given.

In the first place, the mean values of observed data on N and AOU in sea water collected in the deep layer, i.e. the second layer described above, on the stations at every 15° interval between 65°S and 10°N along meridional lines of 100°W and 146°W were calculated.

Then, at each station, the value of N_0 was calculated on the basis of Eq. 3. The results of calculation are given in Table 1. As shown in Table 1, the calculated mean values of N_0 agree very well with each other in a wide area of the ocean. Thus, the mean value of N_0 of 20.2 (average standard deviation, $\pm0.3\mu$g atoms liter^{-1}) above mentioned is confirmed. It can be said that the primary concentration of nitrate in sea water is defined as the nitrate concentration when ΔN_b and AOU are zero. In other words, N_0 is the nitrate concentration when there is no oxidation reaction, and no biological production in the ocean. By knowing the value of N_0 and α, N can be calculated using Eq. 3 and observed values of AOU in situ.

(3) Comparison between calculated and observed concentration of nitrate

In Fig. 3, the comparison is made between vertical profiles of observed N (solid line) and calculated N (dots) by using the value of N_0 of 20.2μg atoms liter^{-1}, α of 0.043 and observed AOU value in situ at each station between 65°S and 17°N along the meridional lines of 146°W and 100°W.

As shown in Fig. 3, in the layer below 1 km depth, the agreement between observation and calculation is proved.

As shown also in Fig. 4, compariosns were done between vertical profiles of observed and calculated values of nitrate concentration obtained in the cruises of the R.V. Ryofu-maru of Japan Meteorological Agency (Ry 69-5, Ry 76-6) and the R.V.

Table 1. The primary concentration of nitrate, N_0 in sea water. (unit: μg atoms liter^{-1})

100°W (1–4 km)				146°W (1–4 km)			
	N obs.	AOU	N_0		N obs.	AOU	N_0
65° S	31.8	278	19.9	65° S	31.8	278	19.8
50° S	34.0	328	19.9	50° S	33.5	307	20.3
35° S	35.7	367	19.9	35° S	34.2	327	20.1
20° S	37.0	390	20.2	20° S	35.3	345	20.5
5° S	38.8	432	20.2	5° S	37.8	398	20.7
10°N*	41.3	495	20.0	10°N	40.3	455	20.7

Average N_0, 20.2 ± 0.3

* 1–3 km

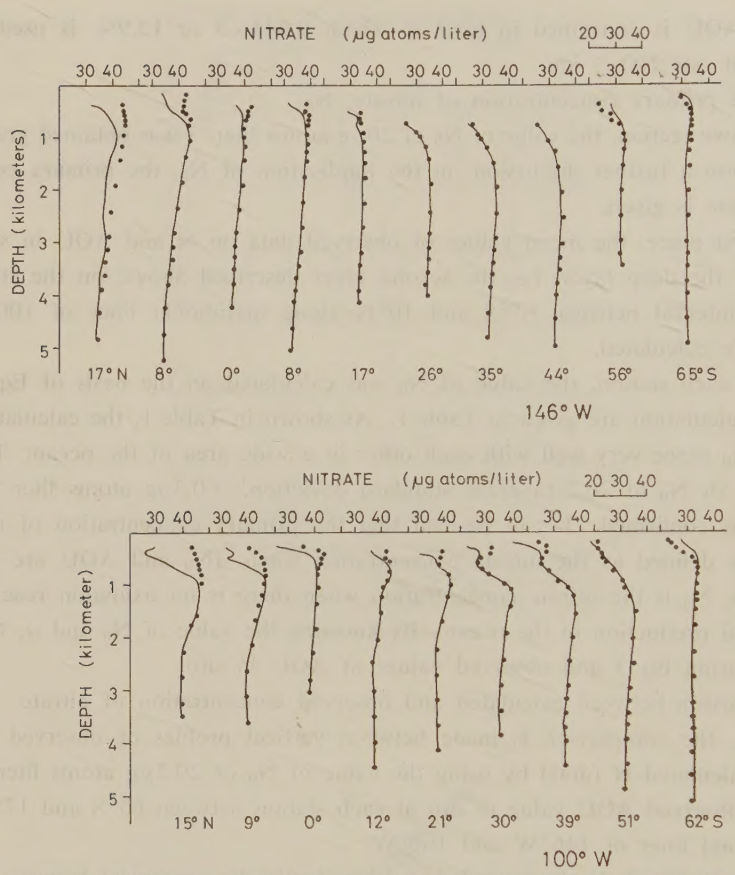

Fig. 3. Comparison between observed and calculated vertical profiles of nitrate in μg atoms liter^{-1}. (solid line: observed values, dots: calculated values)

Hakuho-maru (KH 70-2). The tracks of Ry 69-5 (1969) and Ry 76-6 (1976) were from 48°N to 30°N along 155°E and from 25°N to 10°S along 155°E respectively. The courses of KH 70-2 (1970) were from 51°N to 30°N along 170°W and from 50°N to 17°N along 146°W.

The agreement between calculation and observation is fairly good when the corrections of -6% and $+7\%$ were given respectively to the analytical values obtained during the cruises of Ry 76-6 and KH 70-2. This agreement can be approved when the analytical error of 5% or more is taken into account.

The discrepancy between observed and calculated values of N in the first layer above 1 km depth is due to the loss of nitrate by biological production. Therefore, the observed values of N near the ocean surface are always smaller than calculated values. This difference corresponds to ΔN_b which shows maximum in the subtropical areas of the South and North Pacific. At some stations in the south subtropical areas, the

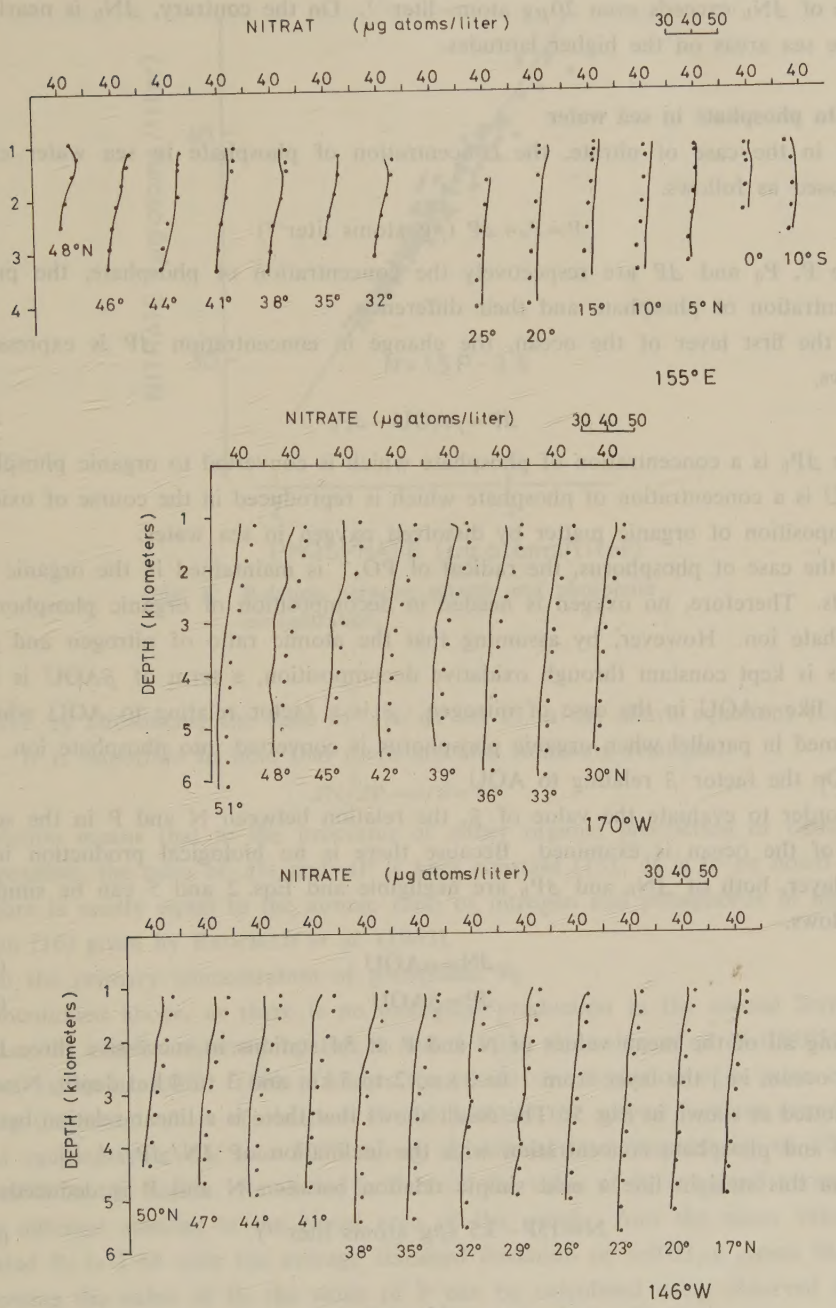

Fig. 4. Comparison between observed (solid line) and calculated (dots) vertical profiles of nitrate in μg atoms liter^{-1} on the cruises of Ry 69-5 (northern part), Ry 76-6 (southern part) along 155°E, and of KH 70-2 along 170°W and 146°W.

value of ΔN_b exceeds even 20μg atoms liter^{-1}. On the contrary, ΔN_b is nearly zero in the sea areas on the higher latitudes.

3. On phosphate in sea water

As in the case of nitrate, the concentration of phosphate in sea water can be expressed as follows.

$$P = P_0 + \Delta P \ (\mu g \text{ atoms liter}^{-1}) \tag{4}$$

where P, P_0 and ΔP are respectively the concentration of phosphate, the primary concentration of phosphate and their difference.

In the first layer of the ocean, the change in concentration ΔP is expressed as follows.

$$\Delta P = \beta AOU - \Delta P_b \tag{5}$$

where ΔP_b is a concentration of phosphate which is converted to organic phosphorus. βAOU is a concentration of phosphate which is reproduced in the course of oxidative decomposition of organic matter by dissolved oxygen in sea water.

In the case of phosphorus, the radical of PO_4^- is maintained in the organic compounds. Therefore, no oxygen is needed in decomposition of organic phosphorus to phosphate ion. However, by assuming that the atomic ratio of nitrogen and phosphorus is kept constant through oxidative decomposition, a term of βAOU is introduced like αAOU in the case of nitrogen. β is a factor relating to AOU which is consumed in parallel when organic phosphorus is converted into phosphate ion.

(1) On the factor β relating to AOU

In order to evaluate the value of β, the relation between N and P in the second layer of the ocean is examined. Because there is no biological production in the deep layer, both of ΔN_b and ΔP_b are negligible and Eqs. 2 and 5 can be simplified as follows.

$$\Delta N = \alpha AOU \tag{6}$$

$$\Delta P = \beta AOU \tag{7}$$

By using all of the mean values of N and P at 54 stations in successive three layers of the ocean, i.e., the layer from 1 to 2 km, 2 to 3 km and 3 to 4 km depth, N versus P is plotted as shown in Fig. 5. The result shows that there is a linear relation between nitrate and phosphate concentration with the inclination of $\Delta N/\Delta P$ of 15.

From this straight line a next simple relation between N and P is deduced:

$$N = 15P - 3.5 \ (\mu g \text{ atoms liter}^{-1}) \tag{8}$$

or

$$P = \frac{N - 3.5}{15}$$

As described above, in the case of nitrate, a factor α or $\Delta N/\Delta$AOU is 0.043. Therefore, a new factor β relating to phosphate and AOU in sea water is estimated to

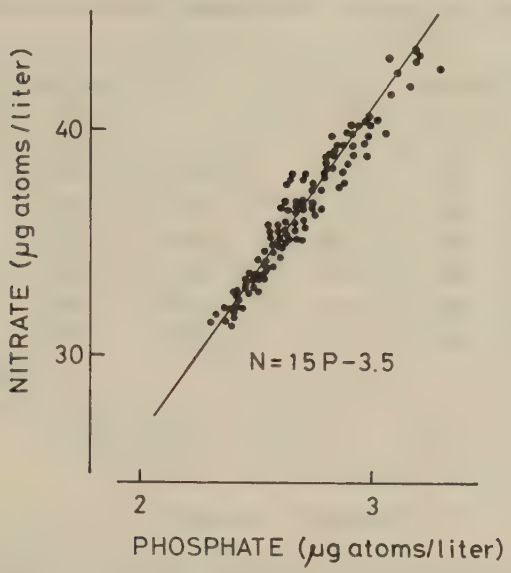

Fig. 5. Relation between nitrate and phosphate concentration.

be 0.0029 by introducing the ratio of $\Delta N/\Delta P$ of 15 in the above equations (Eqs. 6 and 7). It is important to note that there are also following relations,

$$\Delta N/\Delta P = \alpha/\beta = 15 \qquad (9)$$

The relation means that in the processes of either organic production or oxidative decomposition, the ratio of ΔN and ΔP is kept constant (15). It is to be noted that this figure is nearly equal to the atomic ratio of nitrogen and phosphorus in marine plankton (16) given by REDFIELD *et al.* (1963).

(2) On the primary concentration of phosphate, P_0

As mentioned above, as there is no biological production in the second layer of the ocean, P_0 can be obtained by Eqs. 4 and 5 using the value of β of 0.0029 and observed values of AOU. Table 2 shows the results of calculation of a value of P_0 by using the mean values of observed P and AOU in the second layer at every 15° interval ranging from 65°S to 10°N along meridional lines respectively of 100°W and 146°W in the Pacific. As shown in Table 2, the value of P_0 is a good agreement among different stations in the broad area of the ocean. And the mean value of calculated P_0 is 1.58 with the average standard deviation of $\pm 0.03 \mu$g atoms liter^{-1}. By knowing the value of P_0 the value of P can be calculated using observed AOU values.

(3) The comparison between calculated and observed concentration of phosphate

In Fig. 6, the comparison is made between vertical profiles of observed and calculated values of P using observed values of AOU, P_0 of 1.58μg atoms liter^{-1} and β

Table 2. The primary concentration of phosphate, P_0 in sea water. (unit: μg atoms liter^{-1})

100°W (1–4 km)				146°W (1–4 km)			
	P obs.	AOU	P_0		P obs.	AOU	P_0
65° S	2.40	278	1.59	65° S	2.40	278	1.59
50° S	2.50	328	1.55	50° S	2.48	307	1.59
35° S	2.65	367	1.59	35° S	2.53	327	1.58
20° S	2.73	390	1.60	20° S	2.62	345	1.62
5° S	2.83	432	1.58	5° S	2.70	398	1.55
10°N*	2.95	495	1.51	10°N	2.88	455	1.56

Average P_0, 1.58±0.03

* 1–3 km

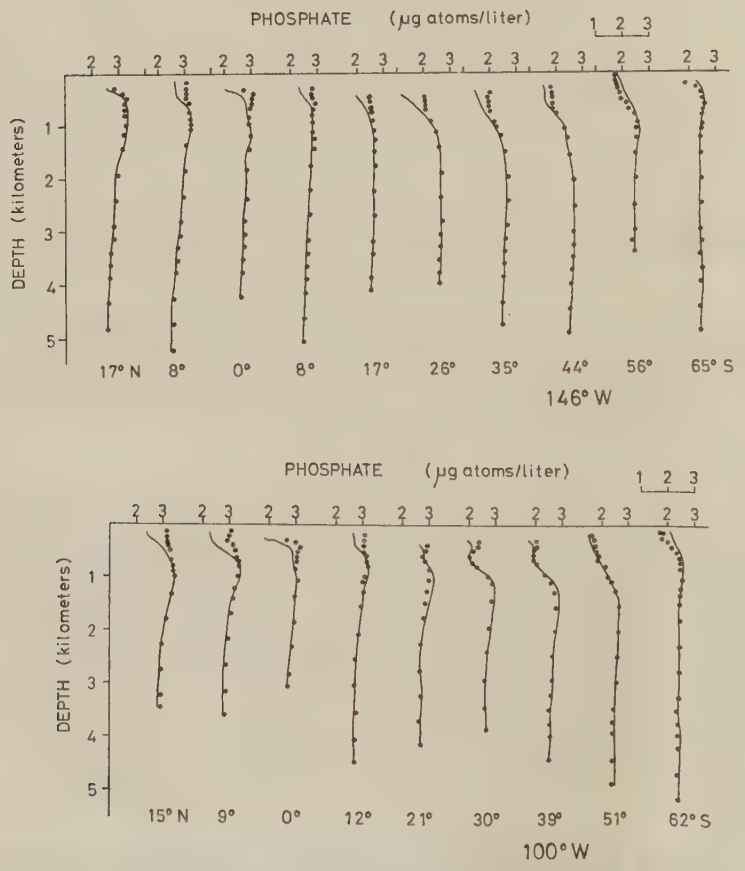
PHOSPHATE (μg atoms/liter)
1 2 3
DEPTH (kilometers)
17° N 8° 0° 8° 17° 26° 35° 44° 56° 65° S
146° W
PHOSPHATE (μg atoms/liter)
1 2 3
DEPTH (kilometers)
15° N 9° 0° 12° 21° 30° 39° 51° 62° S
100° W

Fig. 6. Comparison between observed and calculated vertical profiles of phosphate in μg atoms liter^{-1}. (solid line: observed values, dots: calculated values)

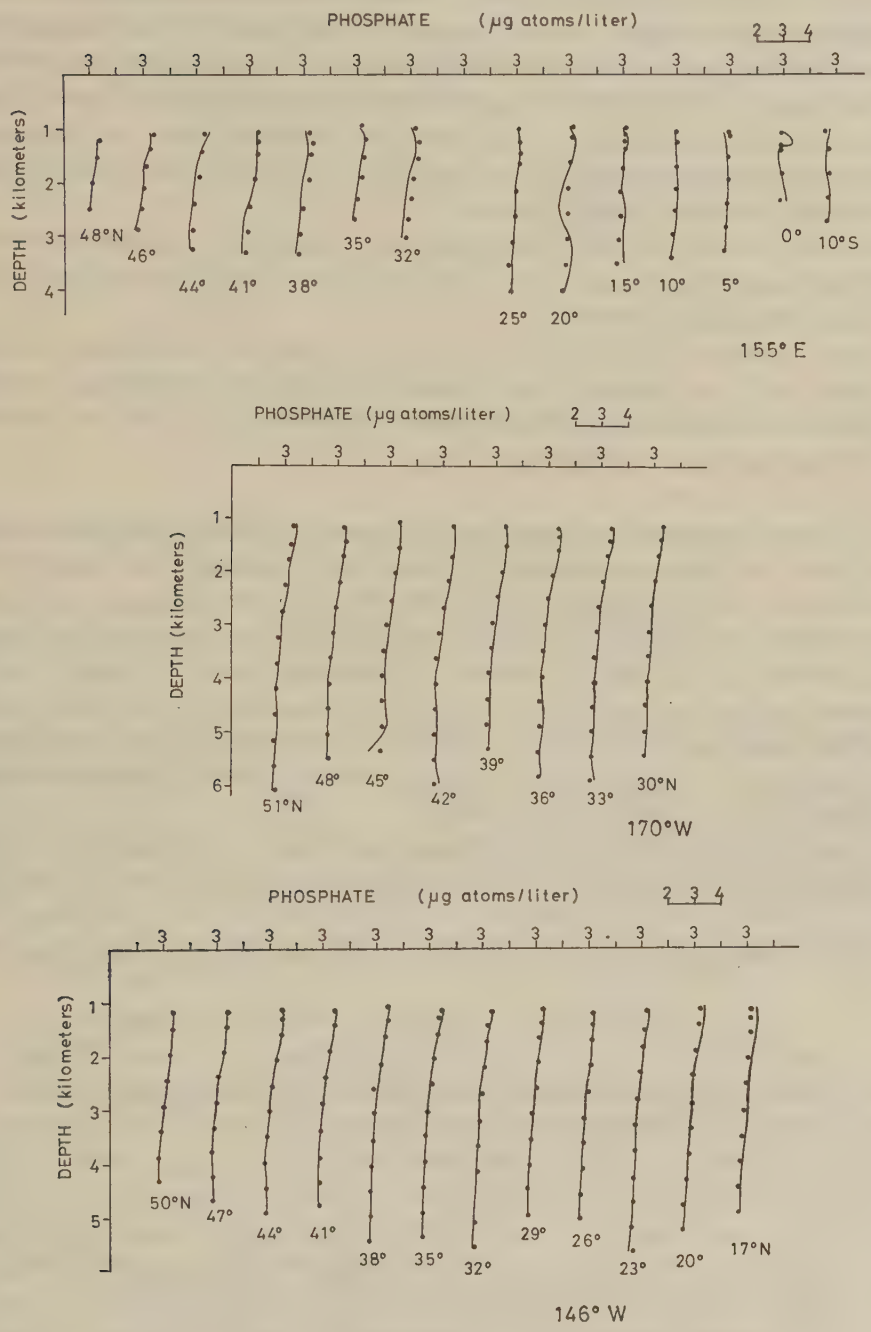

Fig. 7. Comparison between observed (solid line) and calculated (dots) vertical profiles of phosphate in μg atoms liter^{-1} on the cruises of Ry 69-5 (northern part), Ry 76-6 (southern part) along 155°E, and of KH 70-2 along 170°W and 146°W.

of 0.0029 at the same stations as above. As shown in Fig. 6, the agreement between observation and calculation is almost complete. As also shown in Fig. 7, comparisons between vertical profiles of observed P and calculated P are done which were obtained on the cruises of Ry 69-5, Ry 76-6 and KH 70-2 which are described above. There is a good agreement between observed values and calculated ones. The discrepancy between observation and calculation in the first layer (0–1 km) is due to the presence of biological production ($\Delta P_b < 0$) there.

Like ΔN_b, the value of ΔP_b is also greater in the subtropic area of the ocean where ΔP_b often exceed 1.5μg atoms liter^{-1}. On the contrary, ΔP_b is nearly zero in the sea area in the higher latitude.

It is to be noted that the ratio of N_0/P_0 is 12.8 which is smaller than the ratio of $\Delta N/\Delta P$ of 15. As explained later in detail, it is found that the difference between the ratios of N_0/P_0 and $\Delta N/\Delta P$ is the cause of wide variation in the ratio of N/P at different locations and depth in the ocean.

4. The mean concentration of nitrate and phosphate in sea water in the Pacific Ocean

In Fig. 8, the mean concentration of nitrate and phosphate in the almost entire Pacific Ocean along the meridional line from 70°S to 50°N are plotted. The mean concentration was obtained by using every observed datum available from the surface to the bottom at each station. Locations of observation stations at which N and P concentration from the surface to the deep were determined, and the names of the respective cruises are shown in Fig. 9. As shown in Fig. 8, both nitrate and phosphate are a little lower in concentration in the South Pacific than those in the North Pacific and there are the minima at around 35°S.

In the North Pacific, there are the maxima and minima in concentration of both elements respectively around 15°N in the tropical, and around 30°N in the sub-

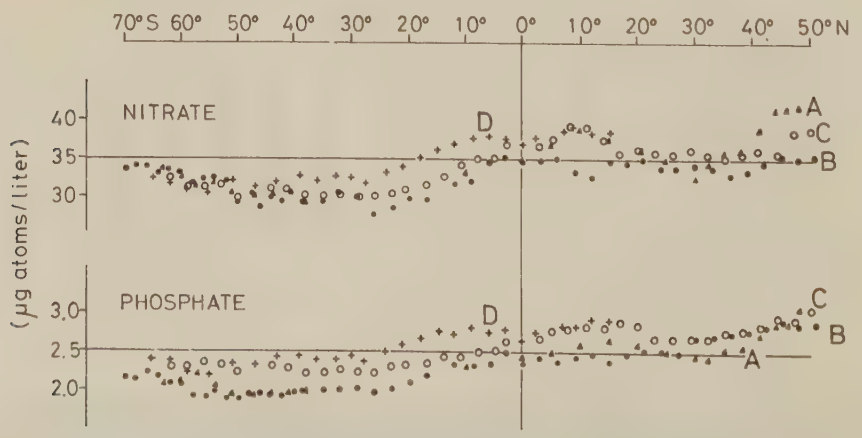

Fig. 8. Mean values of nitrate and phosphate in μg-atoms liter^{-1} in sea water from the surface to the bottom at A, B, C, and D lines in Fig. 9.

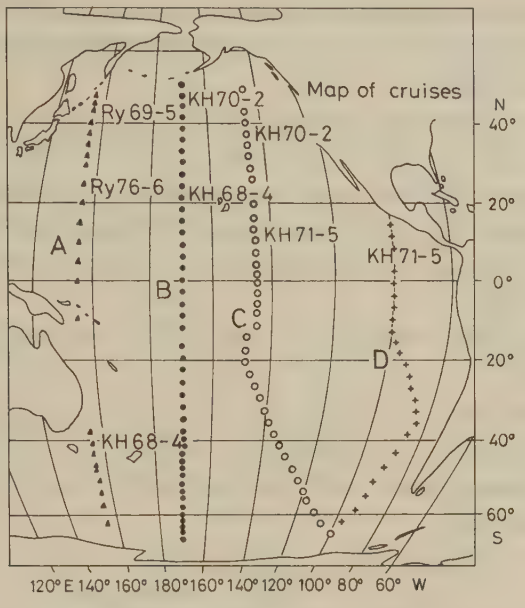

Fig. 9. Cruises and observation stations at which N and P were analyzed from the surface to the deep.

tropical areas. And then nitrate and phosphate concentrations gradually increase as going to the higher latitude.

Mean concentrations of nitrate and phosphate are estimated respectively to be about 34μg atoms liter^{-1} and about 2.5μg atoms liter^{-1}. The mean ratio of N/P is, therefore, 13.6 which corresponds to the value of AOU of about 300μg atoms liter^{-1}. This agrees well with the mean value of AOU observed in the Pacific. As to the relation between N/P ratio and AOU, explanation will be given in the next chapter.

5. The N/P ratio and the factors controlling it in the ocean

(1) Relation between N/P ratio and other factors

As described in detail in the previous study by one of the present authors (SAGI, 1978), N/P ratio in the Pacific is smaller near the surface while it reachs approximately constant value (13–14) in the deep. There is also a horizontal variation in N/P ratio in the ocean. For example, along 100°W and 146°W lines, the minimum value was observed at the surface near 20°S.

With respect to the cause of variation in N/P, it is explained that the small value of N/P ratio near the surface may be caused by the retardation in reproduction of nitrate as compared with that of phosphate (RYTHER and DUNSTAN, 1971).

On the problem, however, as suggested in the previous chapter, the present authors consider that the reason for the variation in N/P ratio is the difference between N_0/P_0

ratio (12.8) and $\Delta N/\Delta P$ ratio (15) on which explanation is given below.

At first, on the basis of Eqs. 1 and 4, the relation between N/P and P_0 and ΔP can be expressed as follows.

$$\frac{N}{P}=\frac{N_0+\Delta N}{P_0+\Delta P}=\frac{12.8P_0+15\Delta P}{P_0+\Delta P}=12.8+2.2\frac{\Delta P}{P} \tag{10}$$

In the euphotic zone near the ocean surface, owing to biological production, P is smaller than P_0. Therefore, ΔP is negative and N/P ratio tends to a smaller value than 12.8. On the contrary, P is larger than P_0 in the deep layer which brings N/P ratio higher than 12.8.

In the next, the relation between N/P ratio and N and ΔN can be given also as follows.

$$\frac{N}{P}=\frac{N_0+\Delta N}{P_0+\Delta P}=\frac{N_0+\Delta N}{(1/12.8)N_0+(1/15)\Delta N}=12.8+2.2\frac{\Delta N}{N+3.5} \tag{11}$$

In addition, the relation between N/P ratio and αAOU can be written by applying Eqs. 3 and 11 as follows.

$$\frac{N}{P}=12.8+2.2\frac{\alpha AOU}{23.7+\alpha AOU} \tag{12}$$

In Table 3, the calculated values of N/P ratio for P values ranging from 0.4 to 3.4μg atoms liter^{-1} at the interval of 0.2μg atoms liter^{-1} are given. As shown in the table, N/P value changes from 6.3 to 14 with the change of P. In the same way, in Table 4, calculated values of N/P ratio for different N values from 2 to 48μg atoms liter^{-1} at the interval of 2μg atoms liter^{-1} are shown.

The Table 5 shows the results of calculation of N/P ratio in relation to AOU ranging from 100 to 650μg atoms liter^{-1} at the interval of 50μg atoms liter^{-1} of AOU.

As shown in the above three tables, N/P ratio is small when N, P and AOU are small and it increases with the increase of N, P and AOU reaching finally the highest value of 14.

In Fig. 10 the relations between N/P ratio and N, P and AOU are shown. It is of

Table 3. Relation between phosphate concentration and N/P ratio. (unit: μg atoms liter^{-1})

P	N/P	P	N/P
0.4	6.3	2.0	13.3
0.6	9.2	2.2	13.4
0.8	10.8	2.4	13.5
1.0	11.5	2.6	13.6
1.2	12.1	2.8	13.8
1.4	12.5	3.0	13.8
1.6	12.8	3.2	13.9
1.8	13.1	3.4	14.0

Table 4. Relation between nitrate concentration and N/P ratio. (unit: μg atoms liter^{-1})

P	N/P	P	N/P
2	5.4	26	13.2
4	8.0	28	13.3
6	9.5	30	13.4
8	10.4	32	13.5
10	11.1	34	13.6
12	11.6	36	13.7
14	12.0	38	13.7
16	12.3	40	13.8
18	12.6	42	13.9
20	12.8	44	13.9
22	13.0	46	13.9
24	13.1	48	14.0

Table 5. Relation between AOU and N/P ratio. (unit: μg atoms liter^{-1})

AOU	N/P	AOU	N/P
100	13.1	400	13.8
150	13.3	450	13.8
200	13.4	500	13.9
250	13.5	550	13.9
300	13.6	600	13.9
350	13.7	650	14.0

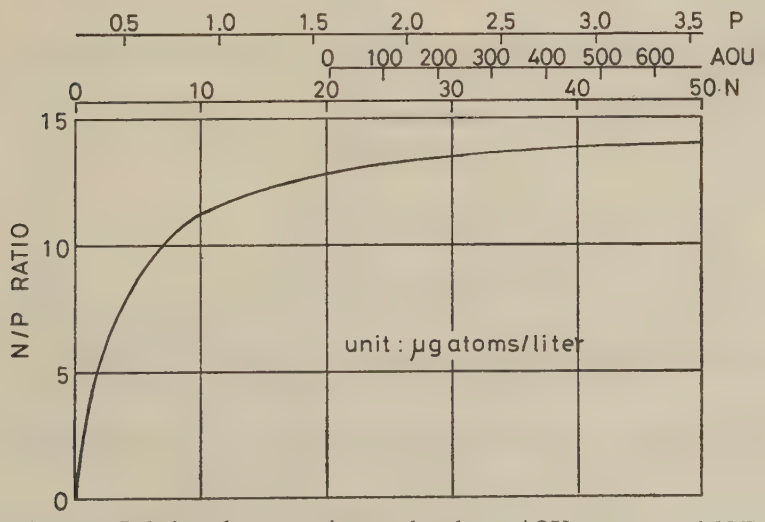

Fig. 10. Relations between nitrate, phosphate, AOU content and N/P ratio.

Table 6. Comparison between observed and calculated values of N/P ratio. (unit: μg atoms liter^{-1})

100°W (1–4 km)				
	N	P	N/P obs.	N/P calc.
65° S	31.8	2.40	13.3	13.5
50° S	34.0	2.50	13.6	13.6
35° S	35.7	2.65	13.5	13.7
20° S	37.0	2.73	13.6	13.7
5° S	38.8	2.83	13.7	13.8
10°N*	41.3	3.00	13.8	13.8

* 1–3 km

146°W (1–4 km)				
	N	P	N/P obs.	N/P calc.
65° S	31.8	2.40	13.3	13.5
50° S	33.5	2.48	13.5	13.6
35° S	34.2	2.53	13.5	13.6
20° S	35.3	2.62	13.5	13.6
5° S	37.8	2.70	14.0	13.7
10°N	40.3	2.88	14.0	13.8

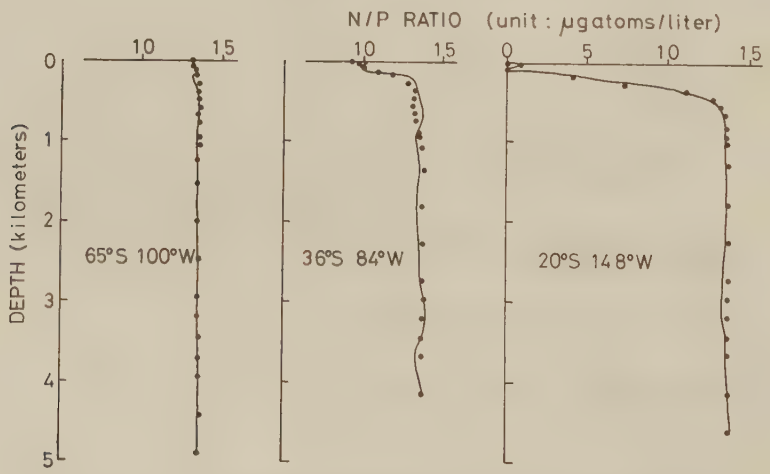

Fig. 11. Comparison between observed and calculated vertical profiles of N/P ratio. (solid line: observed values, dots: calculated values)

importance to note that N/P ratio is determined by any one of the factors of N, P and AOU.

(2) Comparison between calculated and observed N/P values

In Table 6, the comparison is done between mean values of N/P ratio observed

and calculated mean values by using mean values of AOU observed in the second layer on every station at the interval of 15° along meridional lines of 100°W and 146°W. As shown in Table 6, there is a good agreement between observed N/P values and calculated ones.

In Fig. 11, the comparisons between observed and calculated vertical profiles of N/P ratio at three different stations in the South Pacific are shown. The agreement between observation and calculation is almost complete.

In conclusion, it is confirmed that N/P ratio in sea water is a function of either N, P or AOU and the change N/P ratio is caused by the difference between N_0/P_0 ratio (12.8) of the primary concentration of nitrate and phosphate and $\Delta N/\Delta P$ ratio (15) of the amount of change in concentration of nitrate and phosphate in sea water. It is also found that N/P ratio is determined by any one of N, P and AOU in sea water.

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太平洋海水中の硝酸イオンおよびリン酸イオンの生化学的挙動

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海水中の硝酸イオンおよびリン酸イオンは海洋の表層では生物生産によって消費され濃度は低くなり，深層では有機化合物の酸化分解によって濃度は高くなっている。ここで硝酸イオンまたはリン酸イオン濃度は，当初濃度と変化量（±）の和で表わされる。当初濃度とは，生物生産も酸化分解もなく，AOU がゼロの場合の濃度である。

太平洋の 146°W 線および 100°W 線に沿って 65° S から 17°N に至る広い海域で得た硝酸イオン濃度と AOU 値の観測結果から，両者の間に直線関係のあることが確認され，それぞれの変化率の比（$\Delta N/\Delta AOU$）は 0.043，当初濃度は 20.2 $\mu g\,at/\ell$ であることが分った。これらの値を用い，太平洋の広域で AOU 値から硝酸イオン濃度を計算した結果は，海洋の 1000 m 以深では，実測値と計算値の間によい一致がみられた。

またリン酸イオン濃度と AOU 値の変化率の比（$\Delta P/\Delta AOU$）は 0.0029 であり，リン酸イオンの当初濃度は 1.58 μg at/ℓ となった。リン酸イオン濃度についても，計算値と実測値は，1,000 m 以深の広い海域で極めてよく一致した。

海水中の無機形の N/P 比は，無機形の窒素およびリンの当初濃度比（12.8）と，窒素とリンの変化量の比（15）の間に差があることによって変動することが明らかになった。すなわち海洋の表層近くでは，生物生産のために，12.8 より小さくなり，深層ではその比は 14 に近づく。N/P 比の計算結果は，鉛直分布のタイプの異なる場合についても，実測値と計算値はよく一致した。

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Tar ball distribution and dynamics of surface waters in the western North Pacific

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Abstract: In order to consider a feature of mean tar ball distribution in the open ocean, all available data on file at the Japan Meteorological Agency during 1977–1979 were compiled. In general, the waters north of 15°N were extensively polluted with tar balls, while the waters south of 15°N show relatively low contamination with tar balls. Particularly, no contamination was found in the central tropical region. As for the external appearance and size distribution, tars in northern and southeastern regions are characterized by sticky lump with larger size and crumbly grains smaller than 1 mm in diameter, respectively. It is, however, found that the subtropical region shows a wide variability with respect to both external appearance and size distribution as well as concentration. In waters such as the Okhotsk Sea, Oyashio region and northern part of the Coral Sea there exists no tar ball.

It should be noted that even in open ocean the tar distributes heterogeneously and is relatively enriched in a specified region.

By contrasting the dynamics of surface water—geopotential topography—with the tar ball distribution, the findings mentioned above can be consistently interpreted.

1. Introduction

Recently, the marine environment—either coastal region or open ocean—is widely polluted by a multitude of waste desposal from various human being activities. A petroleum contamination, as one of the typical marine pollution, has been recently noted with increasing of the demands on petroleum as the energy source or raw materials for petrochemical industries. This consists of the dissolved/dispersed hydrocarbons, floating particulate petroleum residues (tar ball), oil slicks and so far, all of which have been discharged from the manufacturing processes on land and also appear to come directly from ships.

It is a time to take measure for controlling, preventing and abating the pollution by petroleum containing toxic compounds such as polynuclear aromatic hydrocarbons and heavy metals. Longterm monitoring on petroleum contamination in the ocean environment is needed for evaluating of amounts, distribution and fate in order to assess longterm effects upon various components of the ocean system.

In the Pacific Ocean, especially in the western region including the South China Sea,

the Eastern China Sea and region of the Kuroshio, there exists heavy traffic of maritime transportation including a tanker route. On tanker route, during tank cleaning process, various kinds of hydrocarbons with petroleum origin are possibly discharged into marine environment. On the floating tar ball, many observations were carried out in the North Atlantic (LEVY, 1971, 1979; LEVY and WALTON, 1973, 1976; MCGOWAN *et al.*, 1970) and near-shore region of Japan (MARUMO and KAMATA, 1973; ODATE and HAYASHI, 1973; KOMAKI and MORIOKA, 1975). The monitoring of floating tar ball in the coastal region of Japan was regularly done by the Maritime Safety Agency of Japan. On the other hand, the monitoring of the petroleum pollution including tar ball in the western North Pacific was reported only preliminarily by SANO *et al.* (1979) and SHIGEHARA *et al.* (1979).

Reported here is the tar ball distribution and its relation to general condition of the ocean surface in the western North Pacific and its marginal seas on the basis of the data obtained throughout the Japan Meteorological Agency's ongoing program on the Background Marine Pollution Monitoring in the Open Ocean.

The surveys were done four times a year in the seas adjacent to Japan and twice a year in the western North Pacific by using the network of sampling stations with purpose of monitoring the longterm variation of pollutants and relevant oceanographic parameters.

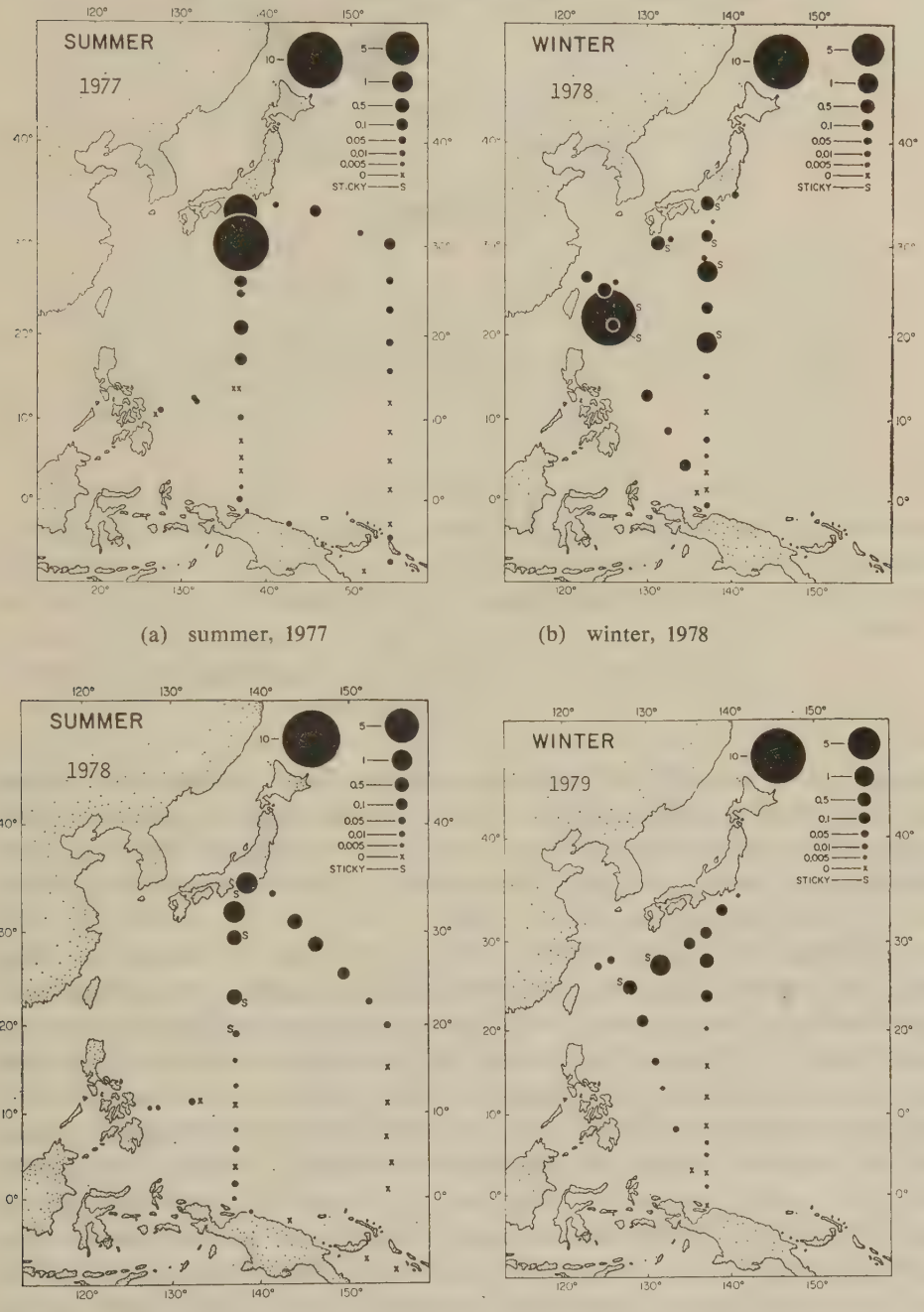
The details in the sample collection were given previously by SANO *et al.* (1979).

2. Results and Discussion

The geographical distribution of tar balls obtained during 1977–1979 is presented in Figs. 1(a)–(e). It is generally seen that tar balls distribute over almost whole area of the western North Pacific, while no tar ball is found in marginal waters such as the Okhotsk Sea, Oyashio region and northern region of the Coral Sea.

As for the distribution of tar balls in the western North Pacific, the trend of the lowering of pollution level with lowering of latitudal position along two meridional lines, 137°E and 155°E, appears. On the other hands, as for the longitudal distribution of tar balls the western margin shows the highest level of contamination which is lowered towards the central subtropical and tropical regions. Seasonal variation in tar ball distribution slightly appears in the case of 137°E line. The southern margin of the region with higher level of tar ball concentration is found to extend down to south to northern margin of the North Equatorial Current. This finding may reflect that the southward transport affects the tar ball distribution in winter monsoon season. The general trends in tar ball distribution mentioned above is well reproduced year to year.

The external appearance of tar balls collected shows site to site variation. Namely, the tar in northwestern and western region are sticky and shiny, while those in southern and southeastern regions are crumbly and dull. The size of tar balls is found to be reduced with lowering of concentration level and reachs down to less than 1 mm in



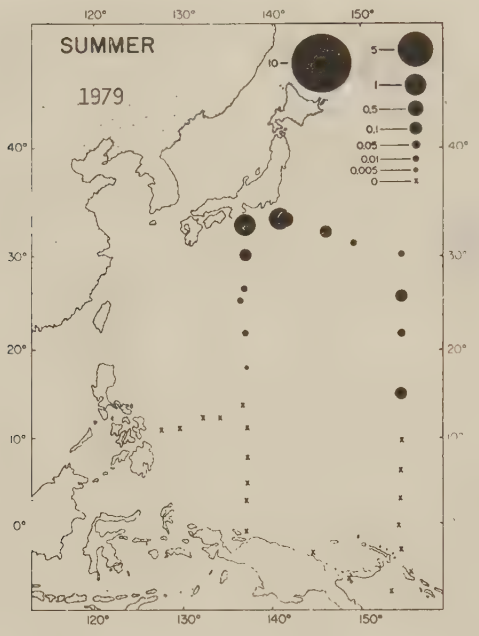
(a) summer, 1977

(b) winter, 1978

(c) summer, 1978

(d) winter, 1979

Fig. 1–1



(e) summer, 1979

Fig. 1–2 Distribution of tar in the western North Pacific: (Unit: mg/m^2)

diameter in the southern and southeastern regions. These findings might indicate that there exists conspicuous regional variation in the degree of weathering of tar which depends on the residence time in the marine environment after its input to the ocean. In subtropical region a wide variability was found in terms of concentration, size and external appearance of tar ball.

The relation of tar ball distribution and oceanic current is considered by using the oceanic monitoring data which were obtained simultaneously. A geostrophic flux upper 1000 m layer is estimated from the dynamic depth anomaly data for each survey along 137°E and 155°E. On the basis of which the latitudal span of each current in the area involved is obtained as listed in Table 1. The patterns of tar ball distribution and oceanic current system along two meridional lines suggest an important role of oceanic current in controlling the distribution of floating pollutants on the ocean surface. For instance, by contrasting the tar ball distribution with the patterns of current direction and geostrophic flux, it is found that relatively higher level of tar concentration appears in the eastward currents independently of the season and year. This could indicate that the tar found on 137°E, in particular, and 155°E was transported by the eastward currents from the region west of each observation line. That is, there could exist the source of tar contamination in the western margin of the western North Pacific.

Table 1. The position of currents in the western North Pacific along the 137° and 155°E lines.

Year	season	line	Currents					
			K	KCC	SW	NEC	ECC	SEC
1977	winter	137°E	32°-29°N	29°-27°N	27°-21°N	21°-7°N	7°-3°N	3°N-
	summer	137°	30°-28°	28°-27°	27°-26°	26°-8°	8°-1°	1° -
		155°			-21°	21°-3°	3°-1°	1° -
1978	winter	137°	31°-29°	29°-27°	27°-23°	23°-5°	5°-2°	2° -
	summer	137°	33°-29°	29°-27°	27°-26°	26°-8°	8°-1°	1° -
1979	winter	137°	31°-29°	29°-27°	27°-21°	21°-6°	6°-3°	3° -
	summer	137°	32°-29°	29°-28°	28°-27°	27°-6°	6°-1°	1° -

K, Kuroshio; KCC, Kuroshio Countercurrent; SW, subtropical waters; NEC, North Equatorial Current; ECC, Equatorial Countercurrent and SEC, South Equatorial Current.

The current data presented above are, being restricted on two meridional lines, not so sufficient to consider the general relation between tar ball distribution and current system over the whole area of the western North Pacific. The longterm mean geopotential anomaly map which appears in the Maritime Environmental Atlas (1975) is compared with an distribution patterns of the tar. The maps of both geopotential anomaly and tar distribution are superimposed altogether in Fig. 2.

A general feature in the geographical distribution and its relation to the general dynamics of surface water clearly appears in Fig. 2. Namely, the floating tar balls are abundant in the Kuroshio, its countercurrent, subtropical waters and the region from east of the Philippines to north of New Guinea, while no tar was found in the region of the North Equatorial Current, main westward current, which is far from highly industrialized region on land and oil tanker route as well as the Okhotsk Sea, Oyashio region and Coral Sea.

The relation in distribution pattern of tar ball and surface current indicates that there exists a main source of tar ball contamination in the northwestern margin of the western North Pacific where a main tanker route is located. The miscellaneous kinds of oils discharged there seems to drift out of marginal waters through the straits or channels to the open ocean. Most of them is likely to be transported toward north-east by the Kuroshio originated east of the Philippines. Other portion probably drifts occasionally down to south, being also affected by the wind system in the area such as monsoon or typhoon.

Tars, being weathered, is then drifted and diverged to various direction according to the related oceanic currents—the Kuroshio Countercurrent and Subtropic Gyre in the northern region, and the Equatorial Countercurrent in the tropical region—, having a close relation with the weather condition in each region.

The regional variations in appearance of tar ball and degree of weathering mentioned above can be consistently interpreted by considering the general circulation of surface

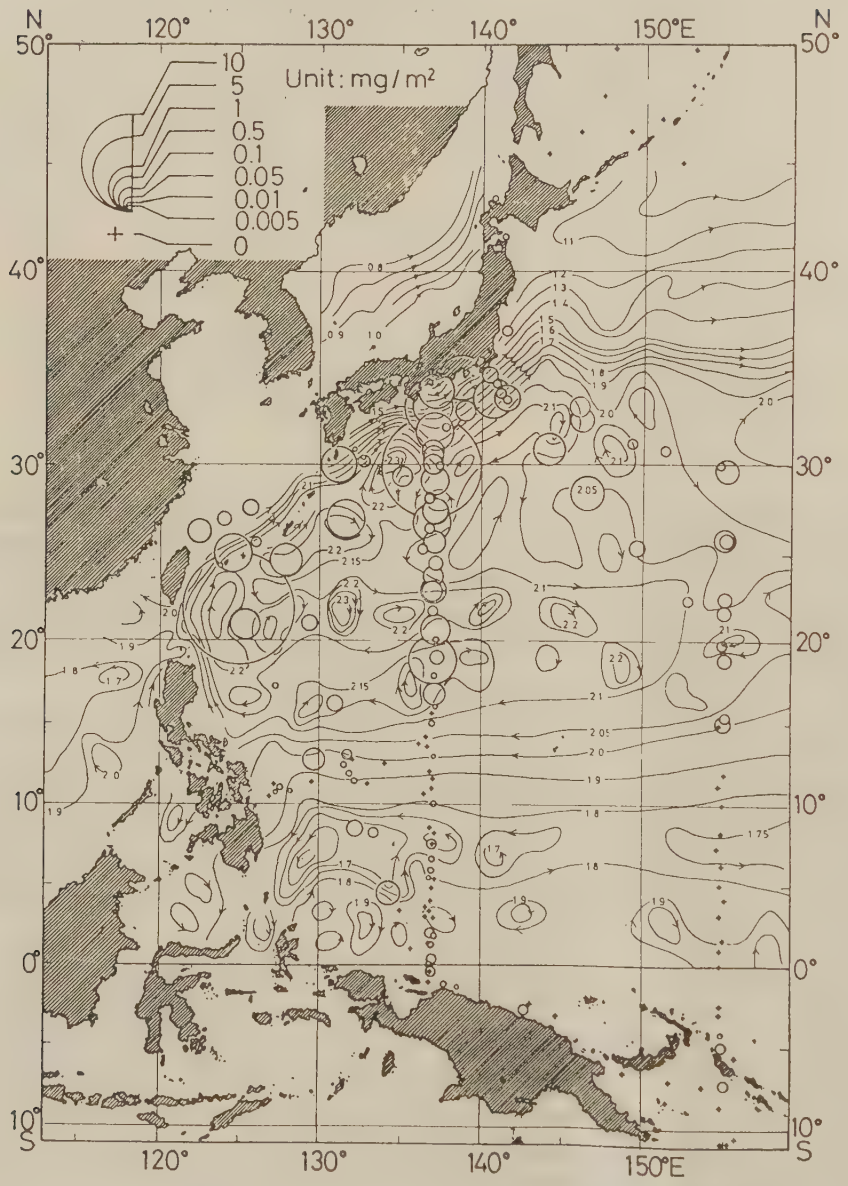


Fig. 2. The geographical distribution of tar in the western North Pacific during 1977–1979 and mean dynamic topography at sea surface (in dyn. m. over 1000 db).

water in the area. That is, the tar in eastern and southeastern regions is much more weathered on account of the longer residence time after its input to marine environments, reflecting the distance from the source of contamination. Especially in the subtropical region, the variability in the distribution of size and concentration is

probably related to structural complexity of the currents in interior subtropical gyre in which subgyres and eddies exist. The weathered tar with smaller size is probably brought from the central subtropical region by the countercurrents or gyres, while the fresh one, crossing over the Kuroshio, probably entered into the subtropical gyre directly.

The ocean currents are complicated because there are irregular eddies, wind currents and tidal currents, superimposed upon the major currents that transport enormous mass of water. Of a great importance is, as far as the tar ball distribution is concerned, that even in the open ocean it distributes heterogeneously and is relatively enriched in a specified region where the convergence of surface currents such as boundaries of currents, peripheries of eddies and so far exists. Such distribution and transfer of tar occur, not randomly, in accordance with a characteristics of the current system such as direction and flux of each current or water as mentioned above. The distribution pattern of tar observed is, as a whole, quite similar to that of floating plastics while is apt to be more affected by the weather condition on account of its lower specific gravity than tar ball (SUZUOKI and SHIRAKAWA, 1979). It should be noted that the tar ball involving other floating pollutants accumulated in a specified region may provide new echological circumstances for marine organisms there and hence the structure of marine community may be altered in future.

As demonstrated here the information on dynamics of surface water of the ocean is very important to understand the mechanism of transportation of tar ball and to make a prediction of future trend of tar ball distribution possible. On the other hands, the tar ball data as well as other floating pollutants could be available for obtaining the information as to general condition of the ocean surface over relatively large ocean area as one of useful parameters.

It is pointed out that further accumulation of the data provides more rigid statistically valid information which could be useful in describing and predicting the behavior of floating pollutants in the marine environment in connection with a general oceanographical condition.

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西部北太平洋のタールボールの分布と海流系

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外洋域におけるタールボールの平均的な分布を知るために，1977–1979年の気象庁による観測資料を検討した。西部北太平洋全体として15°N以北の海域では黒潮およびその反流域に高い濃度がみられ，亜熱帯水域がこれに次いでいる。北赤道海流域の他にオホーツク海，日本海，親潮域などでの濃度は極めて低い。また，外洋域でのタールボールが一様に分布せずに，特定の海域に相対的に濃縮されていることは極めて興味深い事実である。これらのことは西部北太平洋全域の表層水の動態とタールボールの分布を対比することにより，全体としてほぼ矛盾なく説明できることが分った。

The Oceanographical Magazine
Vol. 33, Nos. 1-2, pp. 27 to 42, March 1983

NOTE

Climatology of sea surface temperature in the western North Pacific from 1951 through 1980

Koichi NAGASAKA
Japan Meteorological Agency

The normals and standard deviations of monthly mean sea surface temperature in the western North Pacific Ocean were newly processed based upon *The Ten-Day Marine Report* from 1951 through 1980. The present note is intended to introduce those climatological data in the contour charts.

Requirements for oceanographic information in time series have been increasing year by year from many diverse groups, in particular, those of scientists in climatic researches and forecasts. Although various efforts have been made to maintain oceanographic monitoring network, the oceanographic data in time series for long periods are quite small in volume with exception of sea surface temperature.

Since 1946 the Japan Meteorological Agency has issued the Ten-Day Marine Report to disseminate current oceanographic information at sea surface and subsurface layer in the western North Pacific Ocean. In the reports ten-day mean sea surface temperature charts have been prepared by compiling the data from oceanographic research vessels, marchant ships, fishing boats and airplanes. Since 1977 the sea surface temperature derived from the infrared image obtained from the G.M.S., "Himawari", which is the geostationary meteorological satellite operated by the Japan Meteorological Agency, has been also taken into consideration in the analysis of the sea surface temperature (NAGASAKA, 1982). After expansion of the area for the analysis in several times, now the product covers the waters from 10°N to 53°N in latitude and from 110° to 180°E in longitude.

For many purposes the degree of deviations of sea surface temperature from the long-term means, which is called as "normals", is of value as well as the absolute temperature. The present normals and standard deviations were prepared for the period of 30-year from 1951 through 1980 in the western North Pacific. Although the similar climatological data were prepared in previous for the periods from 1951 through 1960 (MASUZAWA *et al.*, 1962), from 1956 through 1970 (THE JAPAN METEOROLOGICAL AGENCY, 1975) and from 1951 through 1975 (OCEANOGRAPHY DIVISION J.M.A., 1979 and 1980), none of them covered the whole of the western North Pacific and the period of 30-year. The procedure to obtain the climatological data of sea surface temperature is identical with that for the normals and standard devia-

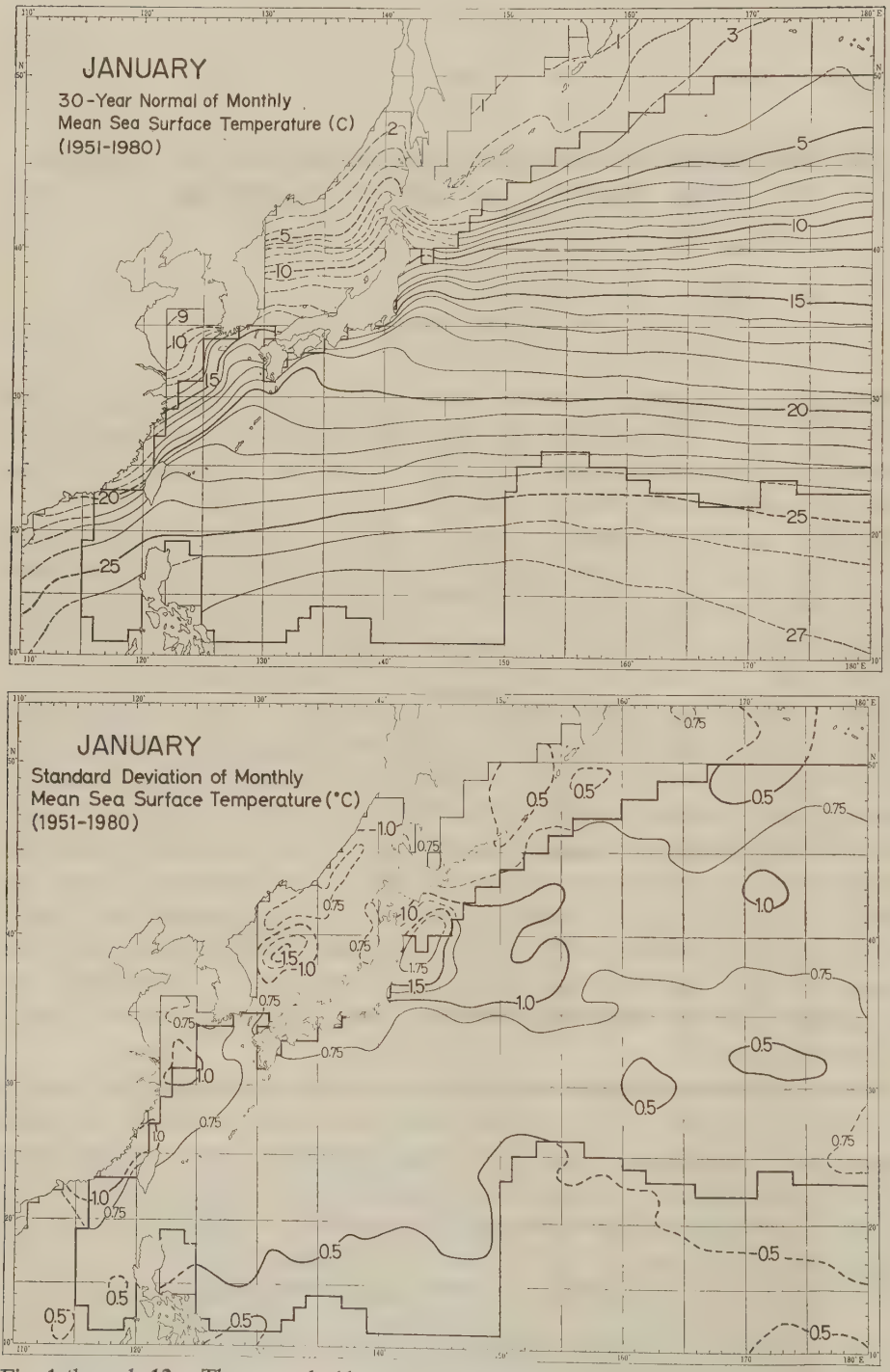
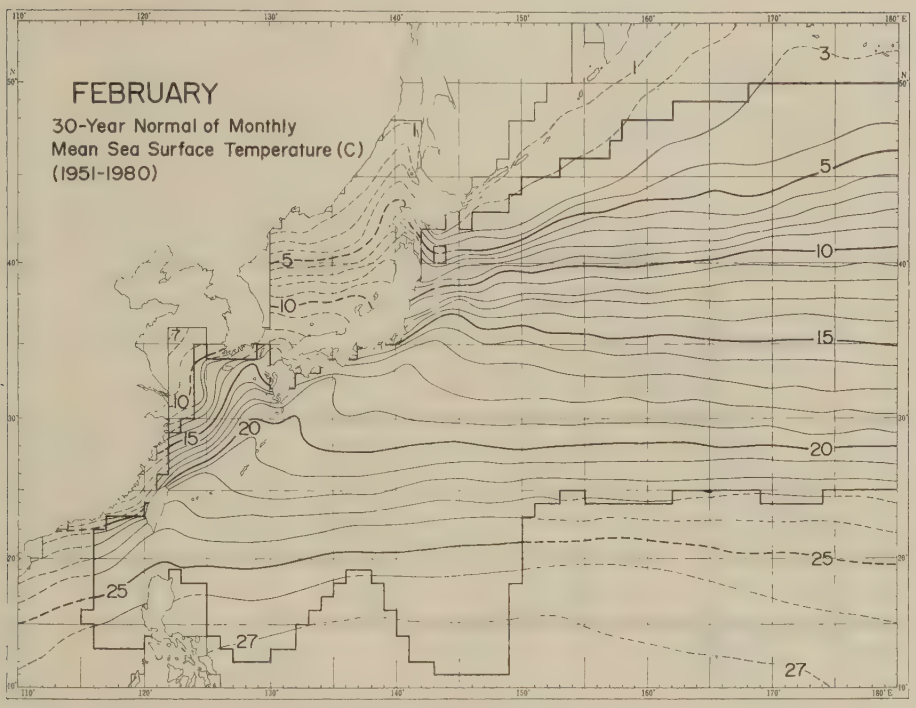
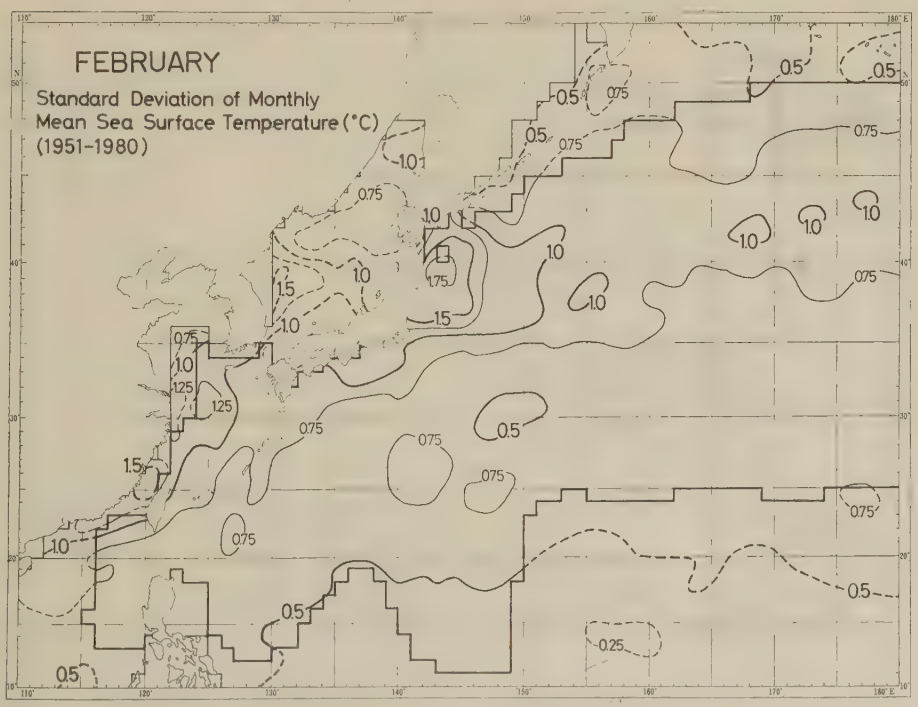
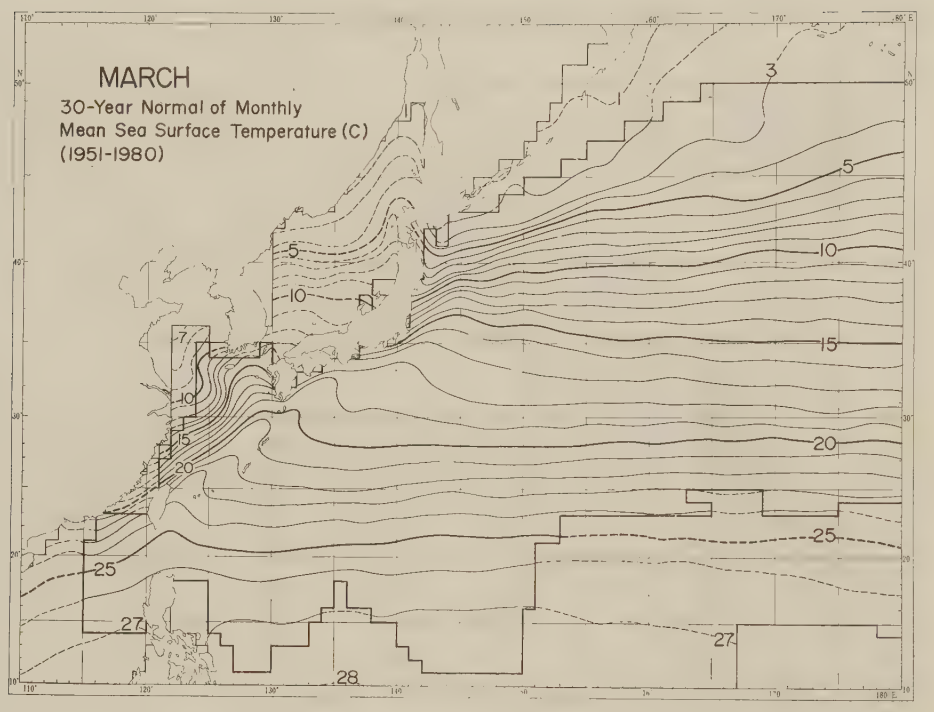
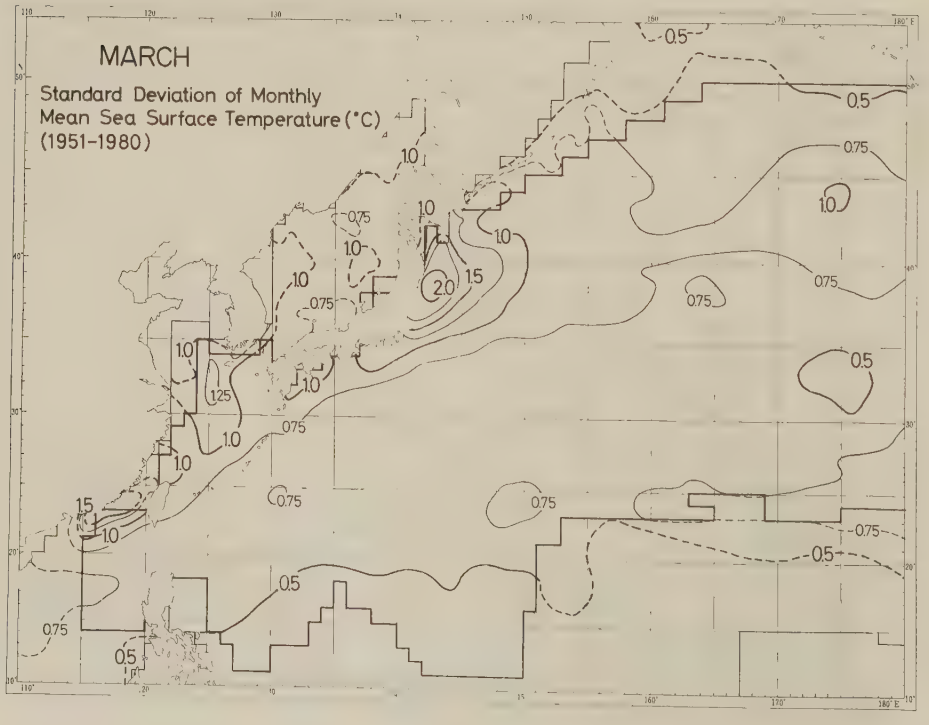


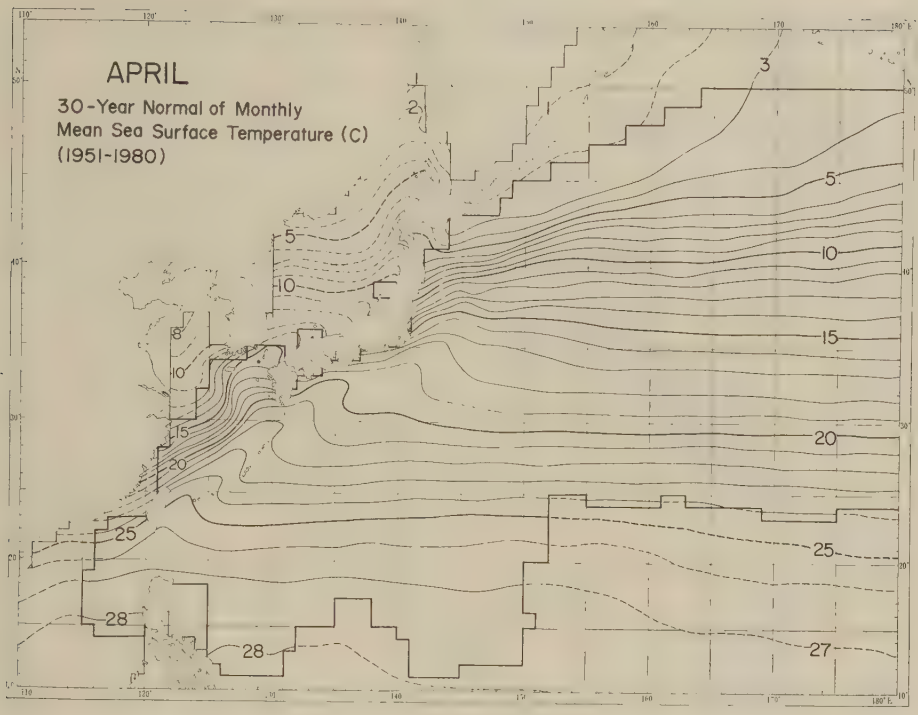
Fig. 1 through 12. The normals (the upper pannel) and the standard deviations (the lower pannel) of the monthly mean sea surface temperature in January through December.

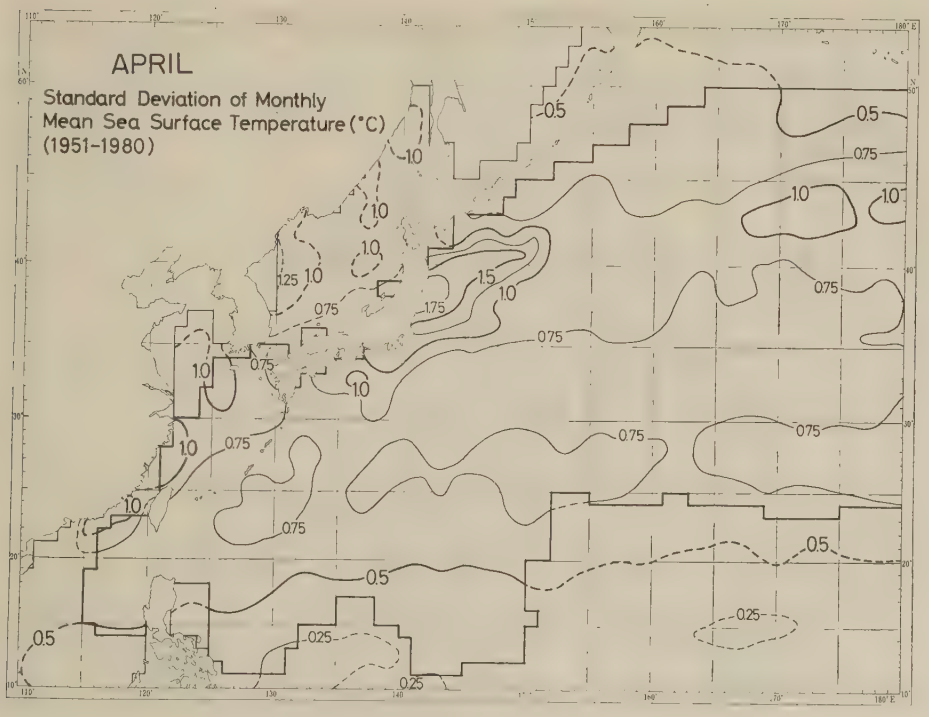

FEBRUARY
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
3
5
10
15
20
25
27

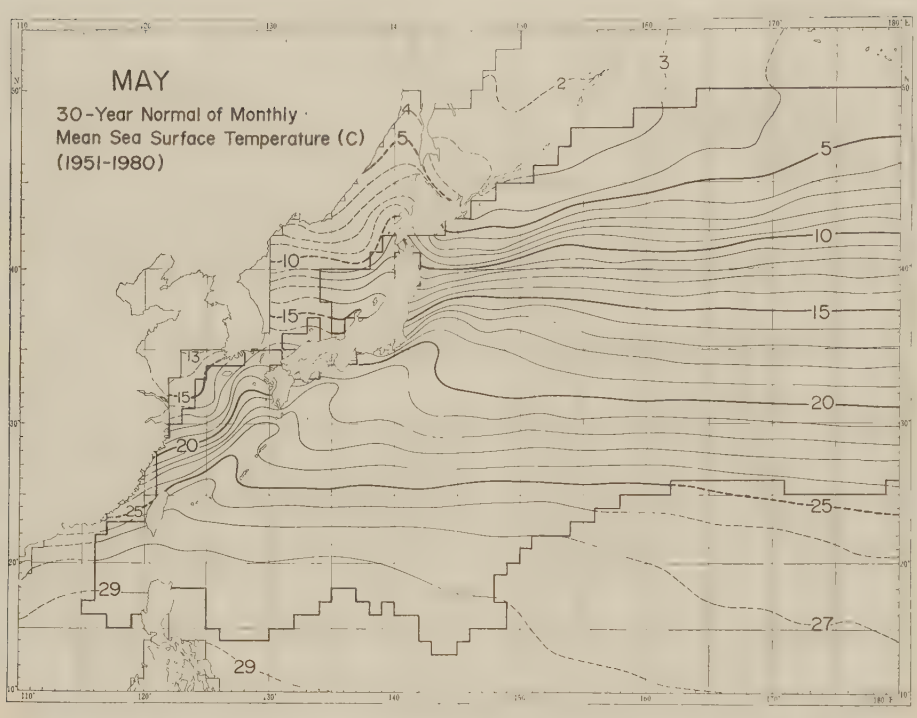

FEBRUARY
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.25
0.5
0.75
1.0
1.25
1.5
1.75

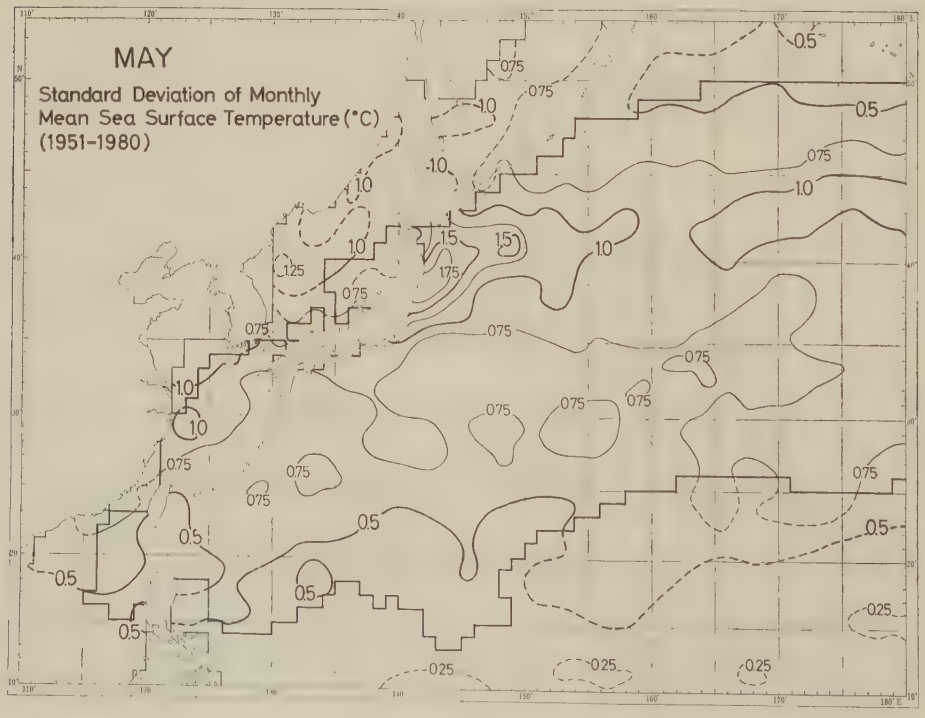

MARCH
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
3
5
10
15
20
25
27
28

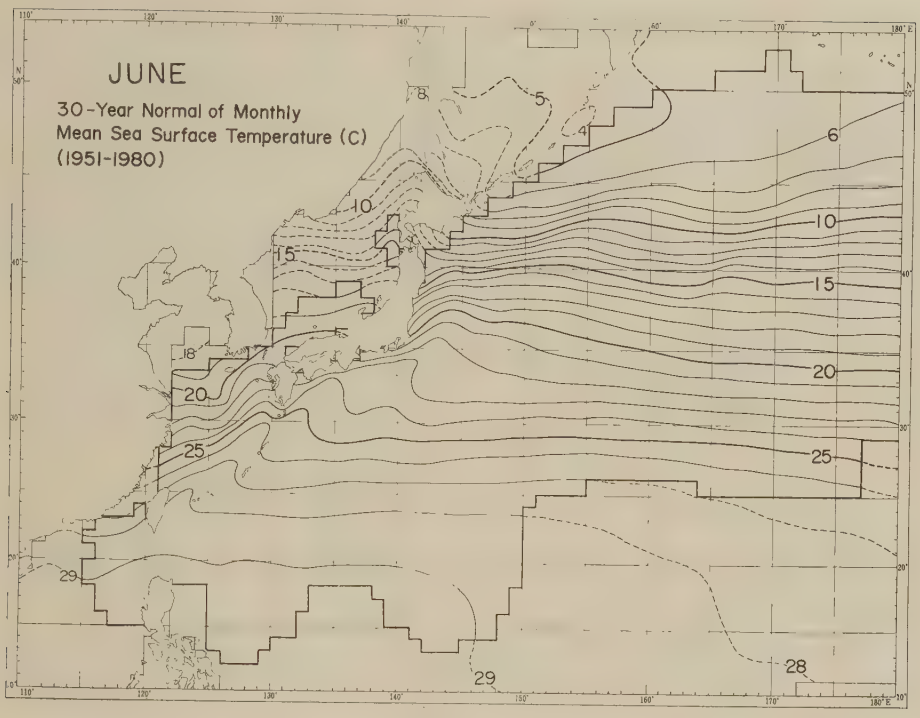

MARCH
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.5
0.75
1.0
1.25
1.5
2.0

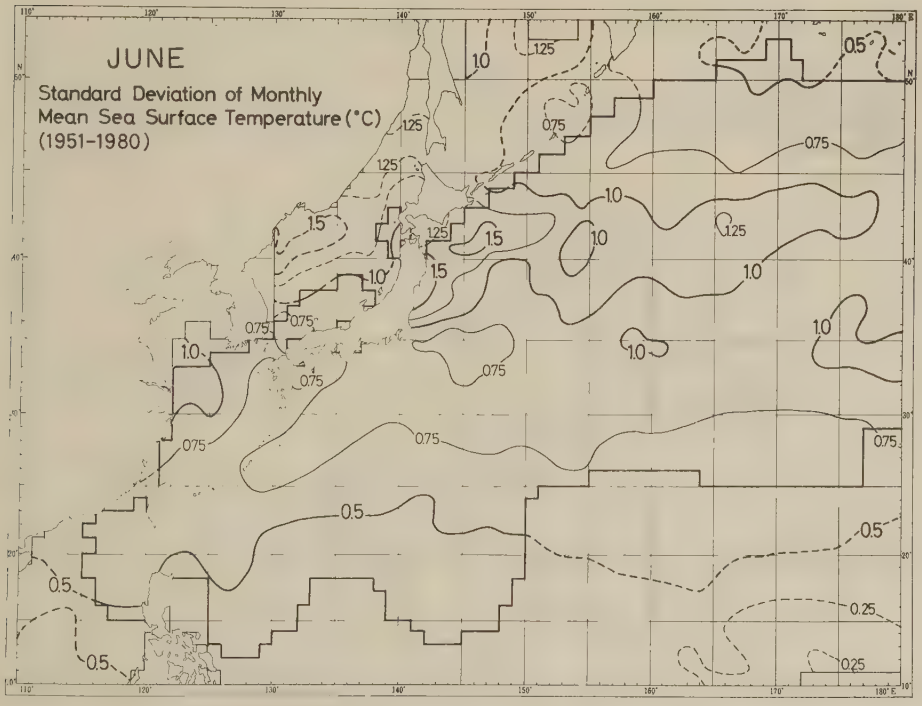

APRIL
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
3
2
5
10
15
20
25
28
27

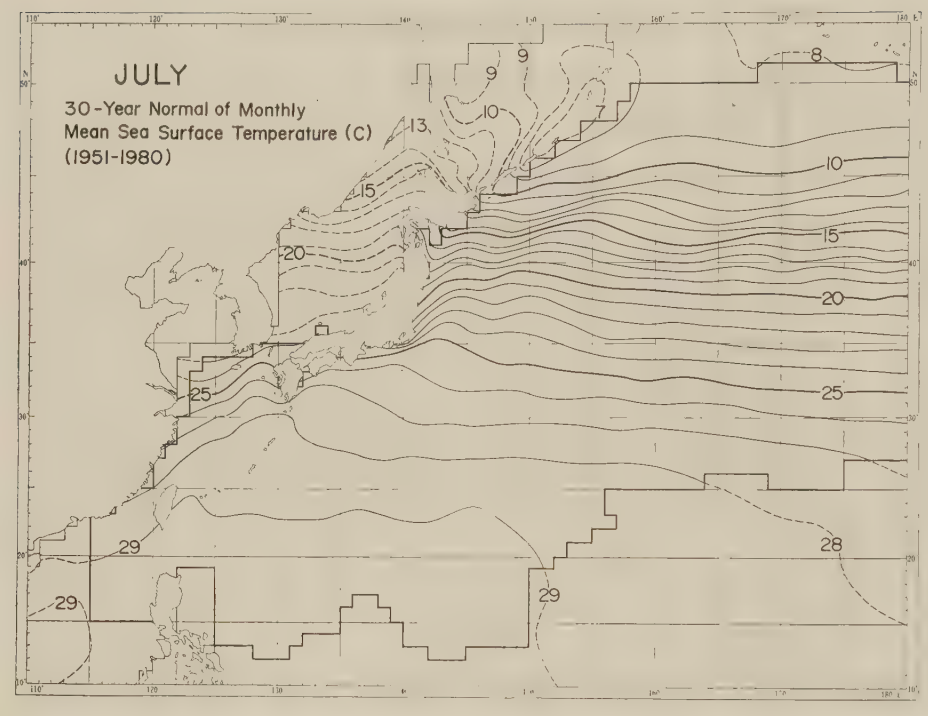

APRIL
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.5
0.75
1.0
1.5
1.75
1.25
0.25

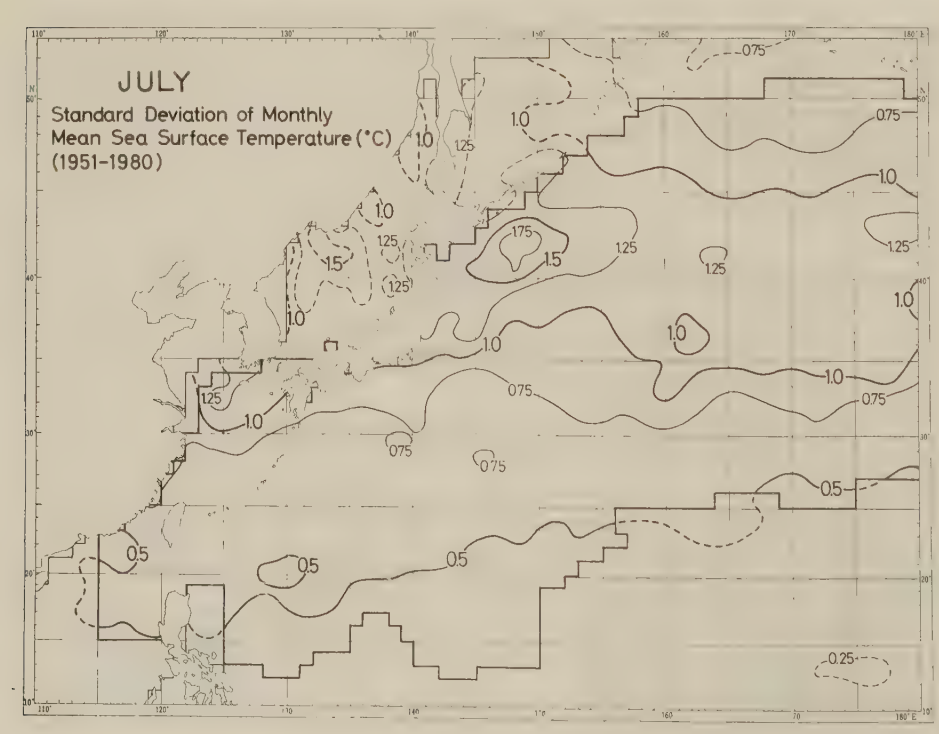

MAY
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)

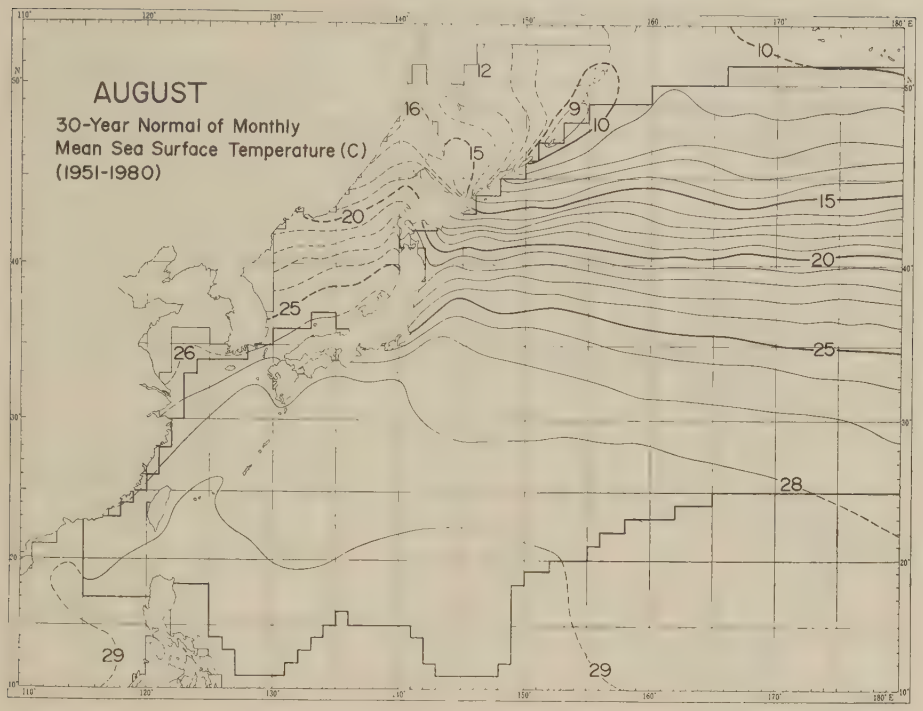

MAY
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)

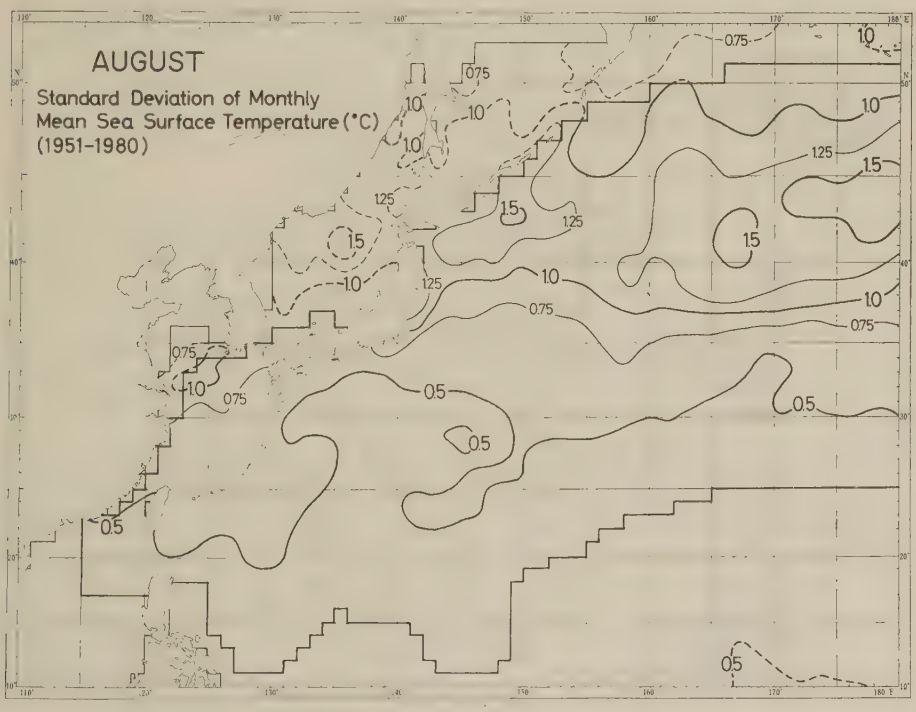

JUNE
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
5
6
10
15
20
25
29
28

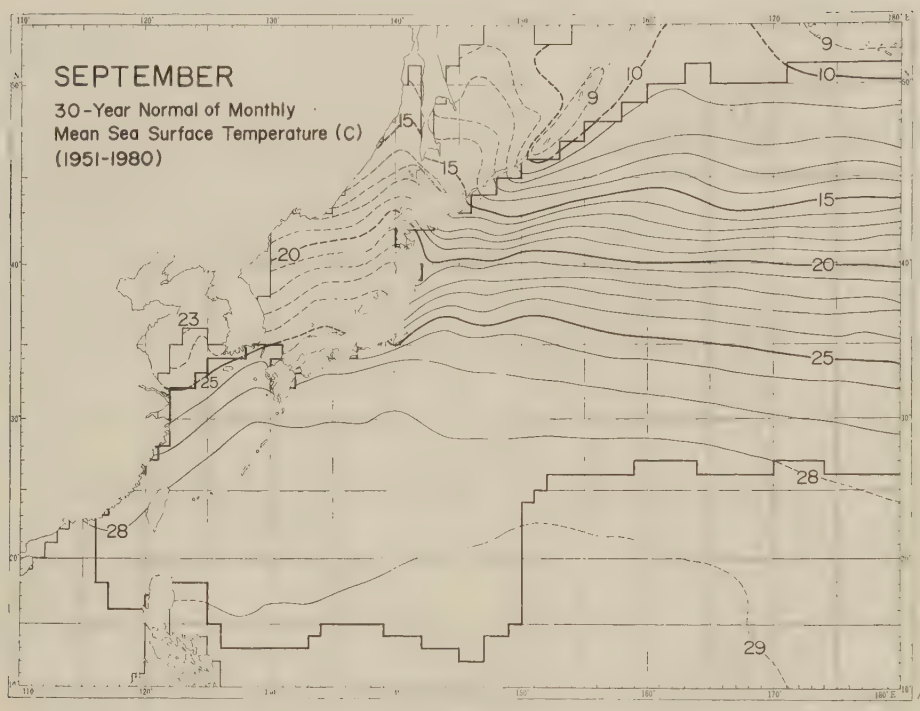

JUNE
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.5
0.75
1.0
1.25
1.5
0.25

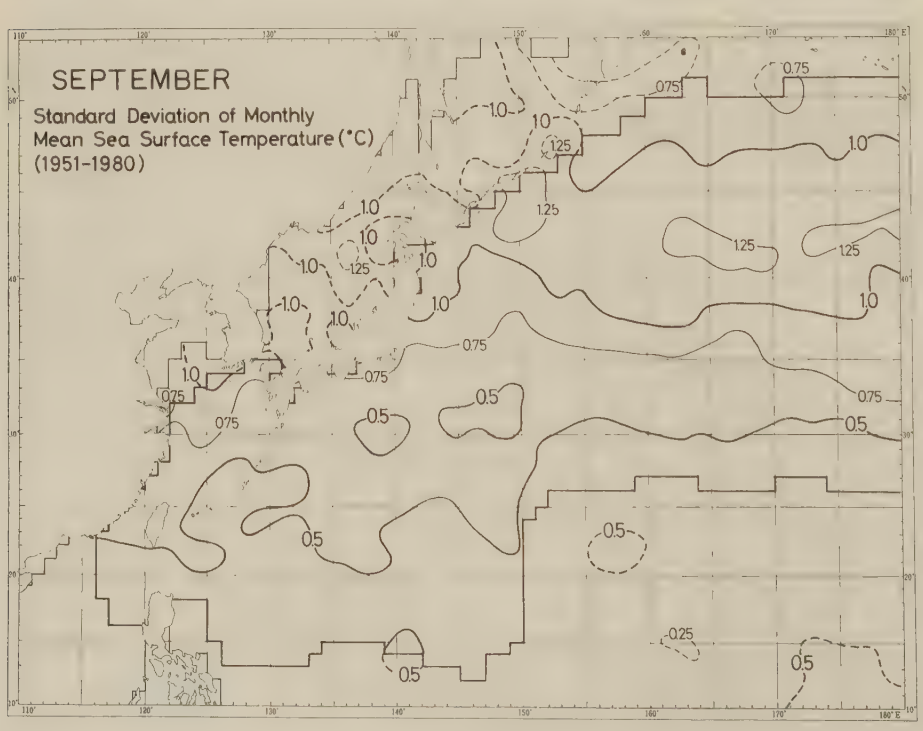

JULY
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
9
9
8
10
13
10
15
15
20
20
25
25
29
28
29
29

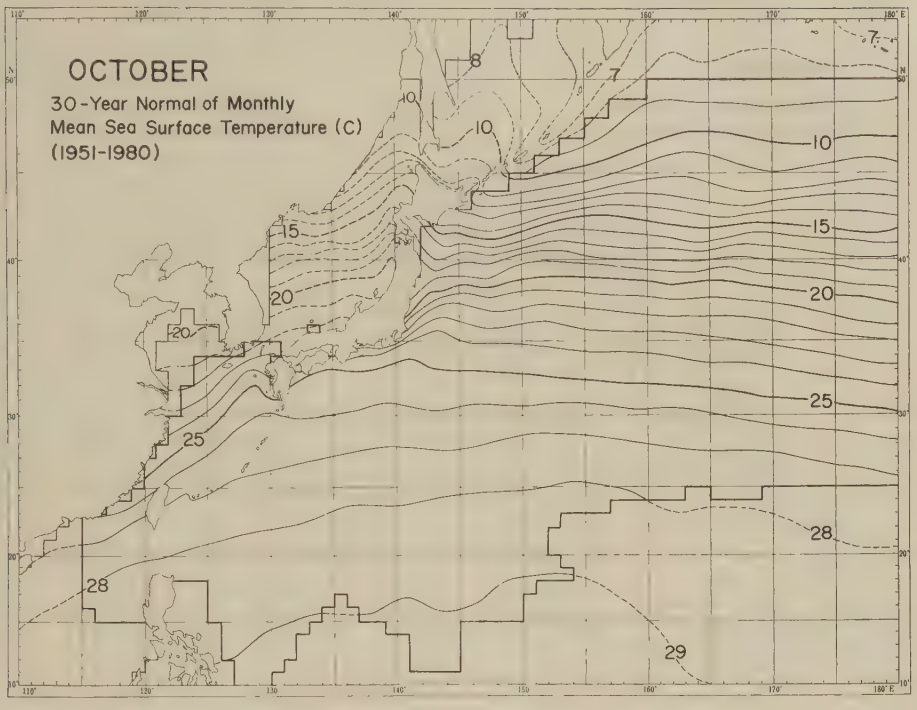

JULY
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
.075
1.0
.075
1.0
1.0
1.25
1.0
1.25
1.5
1.75
1.25
1.25
1.0
1.25
1.0
1.0
1.0
1.0
1.25
.075
1.0
.075
.075
.075
0.5
0.5
0.5
0.5
0.25

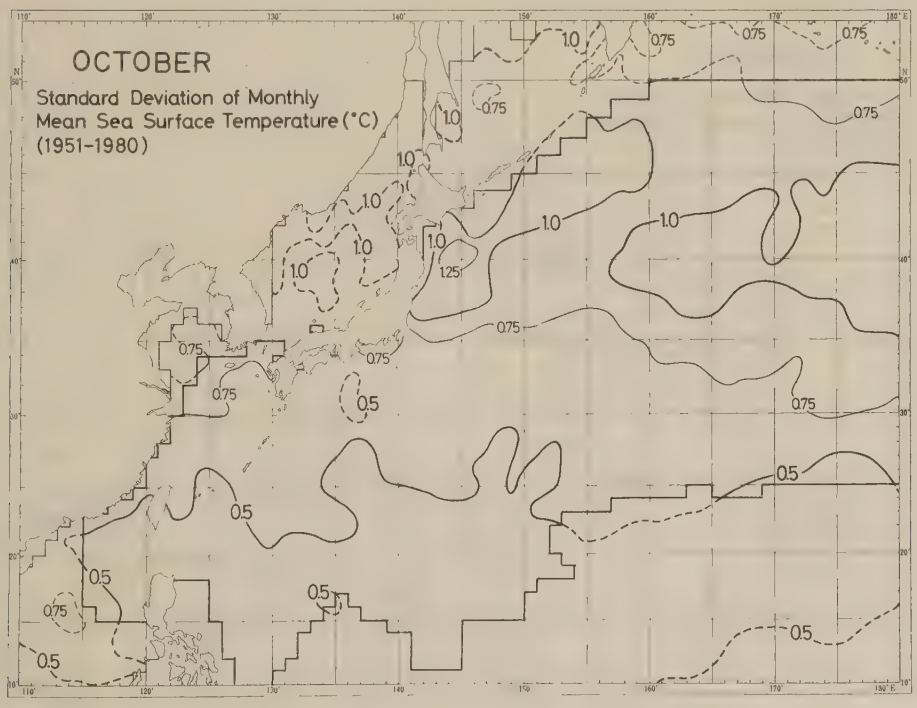

AUGUST
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
10
12
16
9
10
15
20
25
26
15
20
25
28
29
29

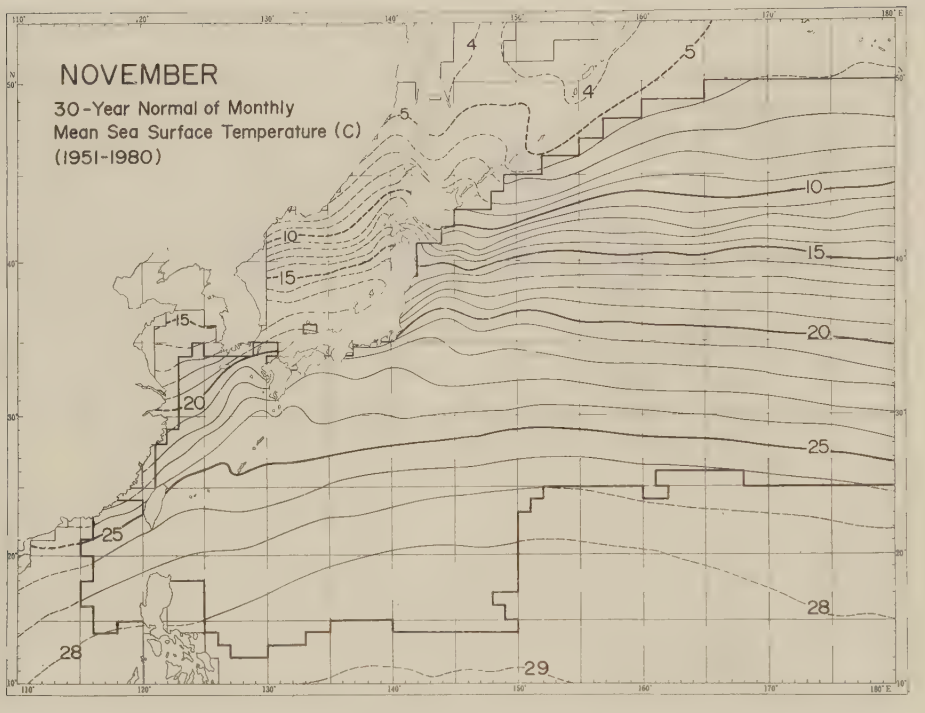

AUGUST
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.75
10
0.75
10
10
10
1.0
1.25
1.5
1.25
1.5
1.5
1.25
1.0
1.0
1.0
0.75
0.75
0.75
1.0
0.75
0.5
0.5
0.5
0.5

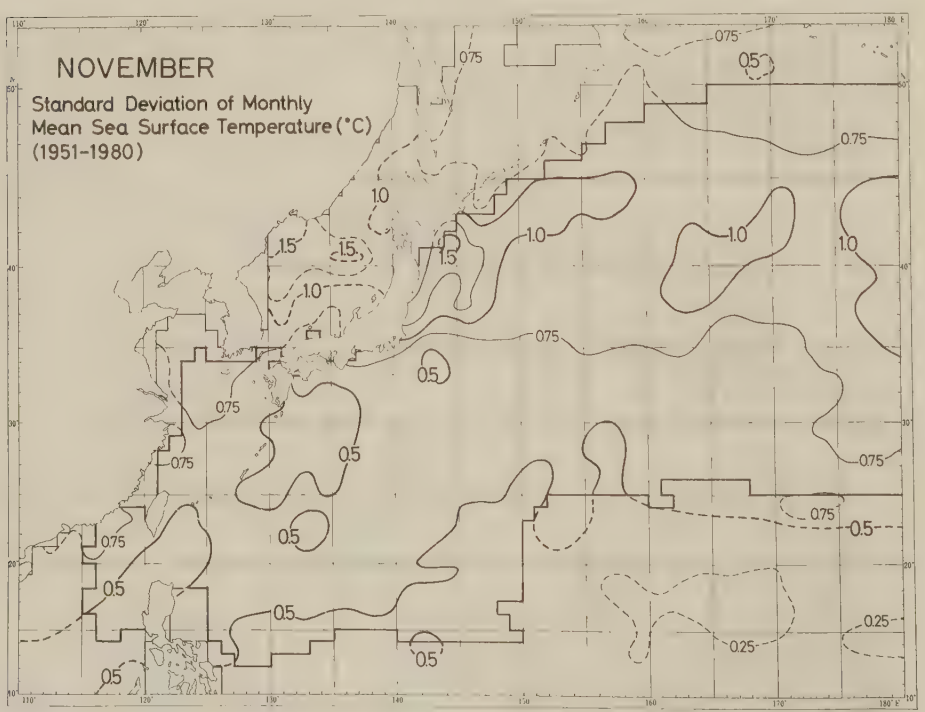

SEPTEMBER
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
9
10
15
20
23
25
28
29

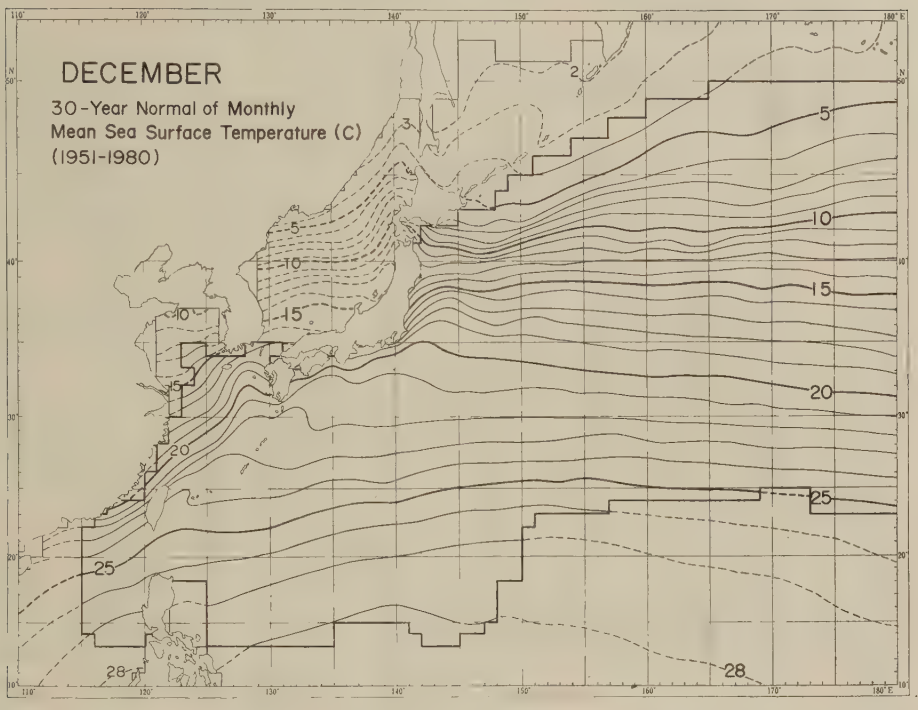

SEPTEMBER
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.75
1.0
1.25
0.5
0.25

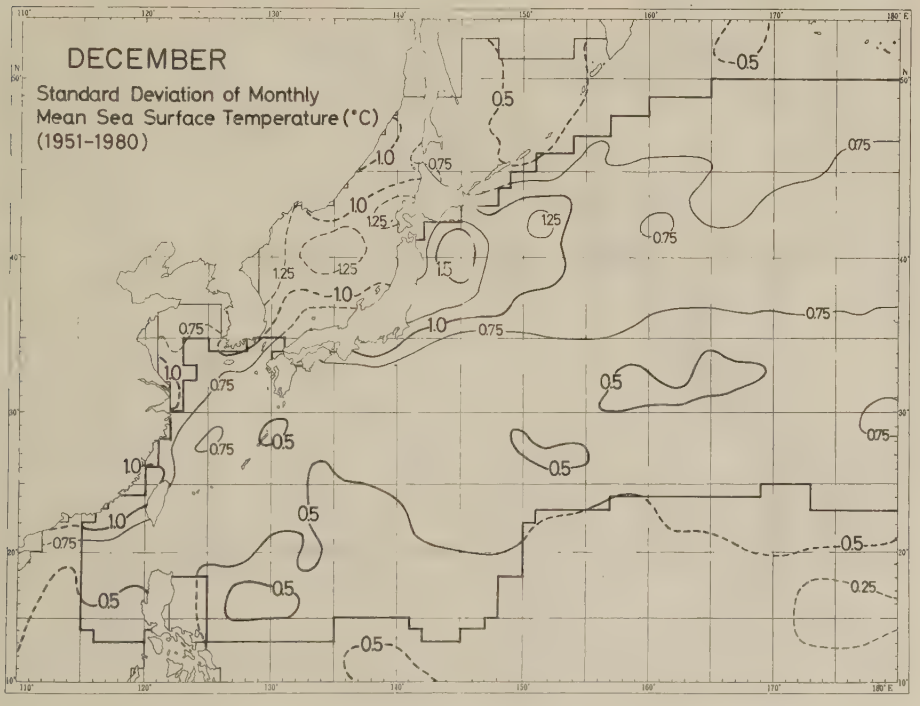

OCTOBER
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
8
7
10
15
20
25
28
29


OCTOBER
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
1.0
0.75
1.25
0.5


NOVEMBER
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
4
5
10
15
20
25
28
29


NOVEMBER
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.75
0.5
1.0
1.5
0.25


DECEMBER
30-Year Normal of Monthly
Mean Sea Surface Temperature (C)
(1951-1980)
2
3
5
10
15
20
25
28


DECEMBER
Standard Deviation of Monthly
Mean Sea Surface Temperature (°C)
(1951-1980)
0.5
0.75
1.0
1.25
1.5
0.25

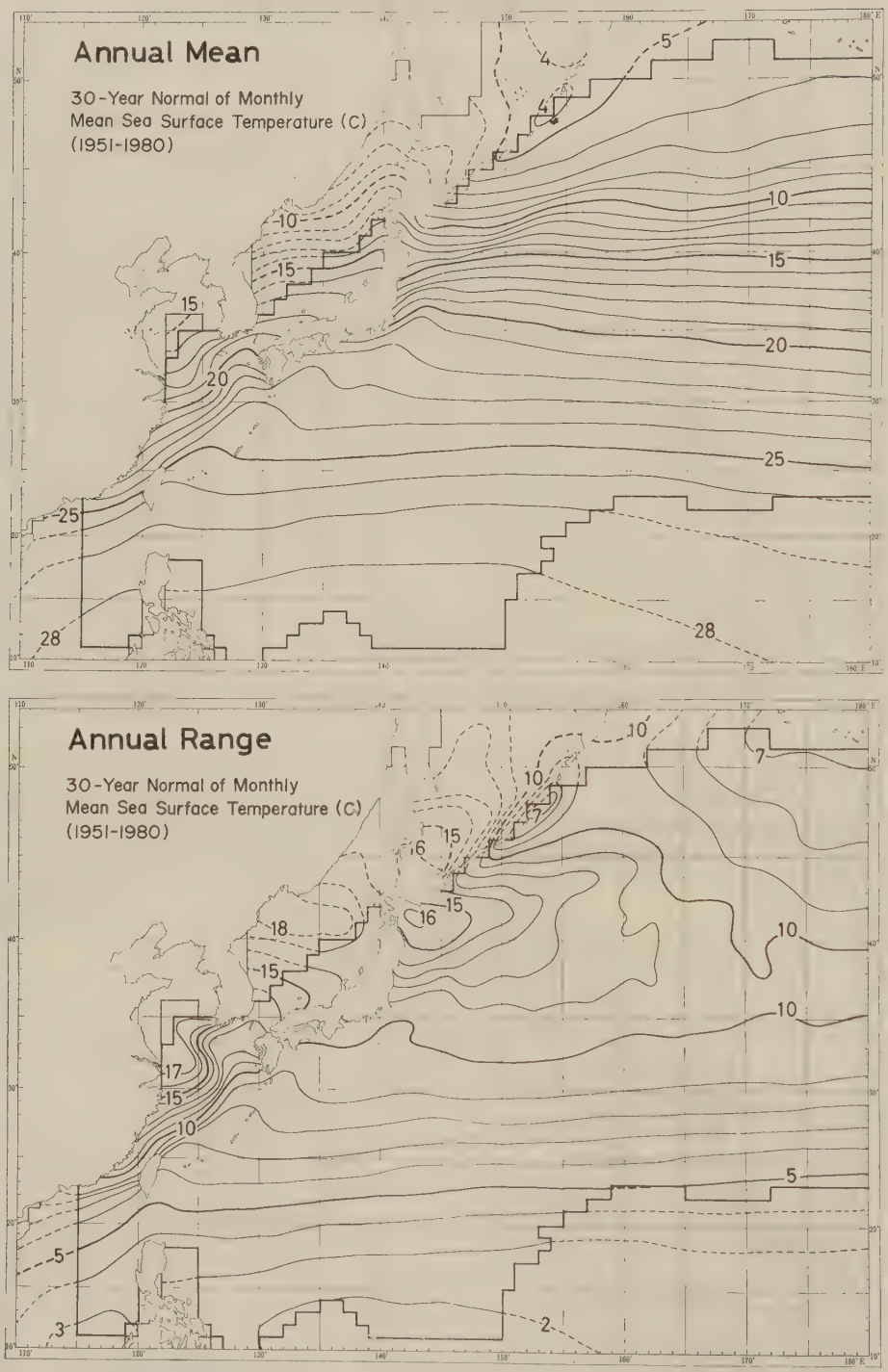


Fig. 13. The annual mean (the upper pannel) and the annual range (the lower pannel) of the monthly mean sea surface temperature.

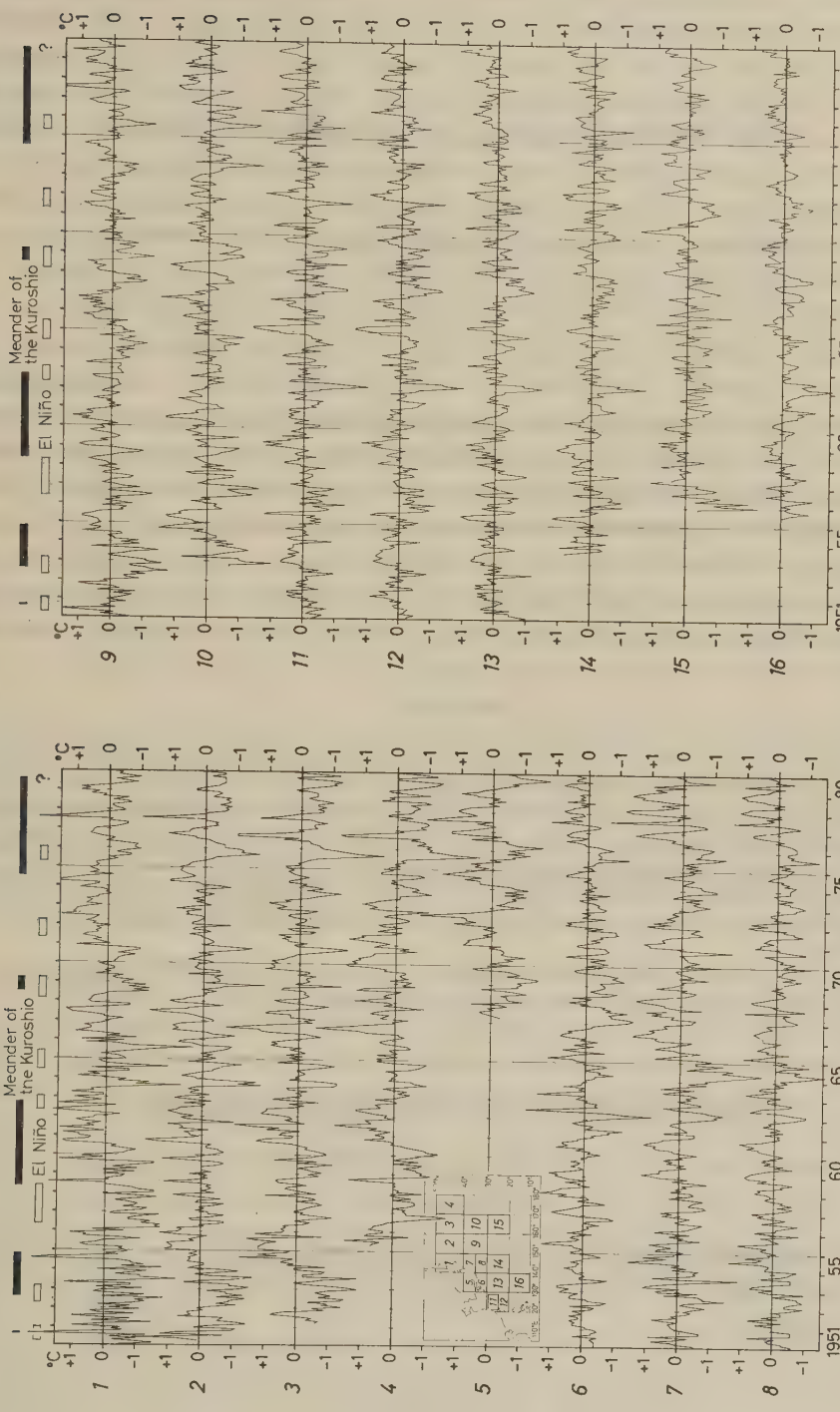


Fig. 14. The time series of the anomalies of the monthly mean sea surface temperature in 5° (2.5°) latitude by 5° longitude squares.

tions for the period from 1951 through 1975. First, monthly mean sea surface temperature in each month from 1951 through 1980 was determined as an arithmetic average of ten-day means. The individual ten-day mean was subjectively estimated from the chart of sea surface temperature to the nearest 1°C before 1974 and the nearest 0.1°C after 1975 at the center of one degree latitude by one degree longitude square. The monthly mean was regarded as missing for the square where two or more ten-day means were not available. The normals of the monthly means were obtained as arithmetic averages of the monthly means of 21 or more years' duration in equal weight. And the standard deviations were determined in the definition of $\sqrt{(T_i-\bar{T})^2/(n-1)}$, where T_i is individual monthly mean sea surface temperature, $\bar{T}$ normal and n number of the monthly means. The processed climatological data are portrated by isopleths at intervals of 1°C for the normals and 0.25°C for the standard deviations (Fig. 1 through 12). The isolines based upon the values less than 24 and more than 7 in numbers are indicated in dotted line. In Fig. 13 the annual mean and range sought on the basis of the normals of twelve months are indicated in the form of chart at intervals with 1°C as well as those of the normals.

Though it is out of the scope of the present note to discuss the details of the climatological data, some of the time series of the anomaly of the sea surface temperature, which is deviation of temperature from the normals, are shown in Fig. 14.

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西部北太平洋における月平均海面水温の累年統計

長 坂 昂 一

(気象庁)

気象庁全国海況旬報に掲載されている北西太平洋の旬平均海面水温図をもとに，海面水温の平年値(1951～1980年，30ヶ年）と月別の標準偏差を求めた。対象海域は10°～53°N，110E～180° で緯経度1度桝目毎に統計した。

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NOTE

Automated analysis of boron in sea water

Tetsuro SUZUOKI, Koji SHIGEHARA and Takeshi YURA
Japan Meteorological Agency

(Received December 1, 1982; Accepted December 16, 1982)

1. Introduction

In our laboratory several inorganic species in many sea water samples are routinely analyzed on board research vessels by using an automated analyzer.

The boron, of which content in sea water is much higher than fresh water, is supposed to be one of the conservative species representative of the open ocean waters. This means that boron is possibly one of the useful parameter distinguishing the contribution of open ocean water on the coastal water including bay and inland sea water. On the other hand the vertical and horizontal distributions of boron are still not described well though it is anticipated to be conservative species of ocean water.

Recently, the automated boron analysis using azomethine H of which availability was first suggested by PETROVSKY (1963) is described for plant tissue (BASSON *et al.*, 1968) and aqueous solution (BASSON *et al.*, 1974). Throughout these previous works it was proved that azomethine H is highly sensitive to boron in the aqueous solution.

The modification and application of the method to boron analysis in the sea water on board the ship are reported here.

2. Experimental

Reagents: Standard solution of boron; 500 mg B/1 stock solution was prepared by dissolving 715 mg of boric acid into 250 ml of distilled water. A series of standard solution was prepared by adding the appropriate amount of stock solution into sea water.

EDTA-2Na- Sodium Acetate solution (reagent B); 8 gr of EDTA (disodium ethylenediammine tetraacetate, dihydrate) and 50 gr of sodium acetate were dissolved in 1 liter of distilled water. The pH of the solution was adjusted to 5.24 with 6N HCl solution. 2 ml of 5% sodium dodecyl sulfate ("Nikkol" SLS) was added to the buffer solution just before using.

Azomethine H—L-ascorgic acid solution (reagent A): 3.6 gr of 1-(salicylideneamino)-8-hydroxy-3, 6-naphthalene-disulfonic acid (Dotite azomethine H) and 8 gr of L-ascorbic acid were stored in a plastic bottle (500 ml) in laboratory on land. The

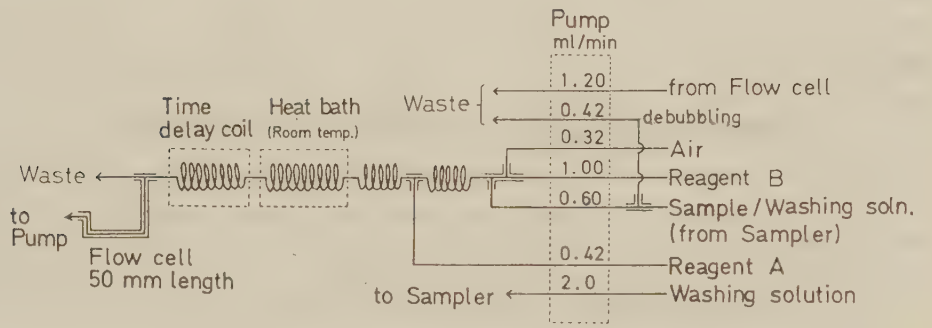

Fig. 1. Flow diagram in automated analysis of boron.

bottle was kept in dark and cool place. On board the ship the 500 ml of distilled water was poured to the bottle, and then the bottle was shaken vigorously and stored in a refrigerator. This solution containing the suspension of azomethine H can be used for at least ten days. An appropriate amount of the solution prepared above was transferred to a glass reagent bottle which is warmed on the water bath until the suspension in the solution completely disappears. This solution should be freshly prepared just before each run of automated analysis.

Washing solution: 3.1 gr of sodium chloride was dissolved into 1 liter of distilled water.

Instrumentation: Standard "Technicon Autoanalyser II" was used as the instrument for automated analysis. A phototube (Technicon 199-B021-01) colorimeter with a 50 mm tublar flowcell and 420 nm filter were used for color detection. Speed of sample analysis is usually 30 samples an hour and the ratio of flow rate of sample to washing solution is fixed to 2:1. Sample cups were washed in every operation by 5% sodium hydroxide solution, distilled water and sample itself. A flow diagram used is illustrated in Fig. 1.

3. Result and discussion

The variables affecting the color formation of azomethine H—boron complex such as pH, concentration of reagents (A and B), ionic strength (salinity), reaction time and so far are considered to get an optimum analytical condition in an shipboard automated analysis.

It has been pointed out in previous work (Sakurai *et al.*, 1979; Basson *et al.*, 1969) that the formation of azomethine H—boron complex is critically affected by the pH of buffer solution (reagent B). The effect of the pH on color development is considered by using two kinds of sea water samples with the salinity of 35 and 28 permil, the latter of which was prepared by diluting the sea water (35 permil) with the distilled water, that is, its boron content is four fifth of original sea water sample.

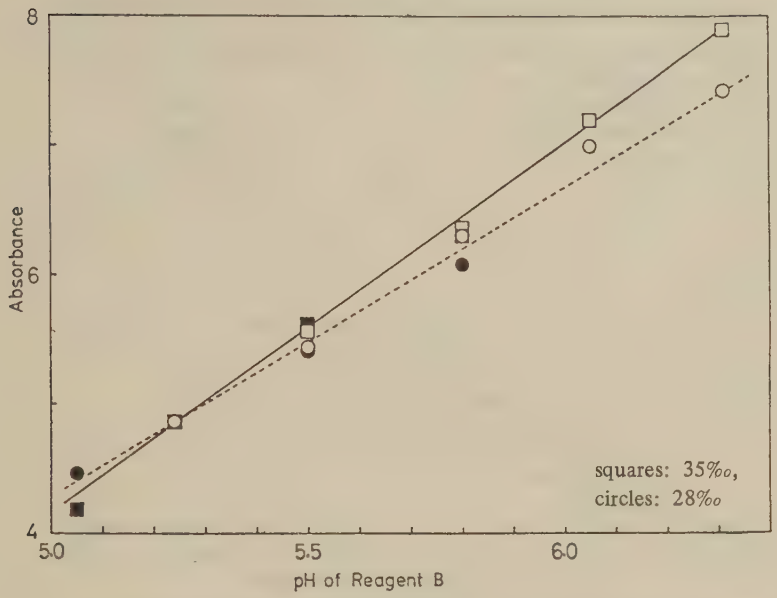

Fig. 2. Relation between absorbance and pH of buffer solution (reagent B).

The relation between pH and absorbance is shown in Fig. 2 where the value of absorbance of B in 28‰ sea water is multiplied by 1.25 in order to convert to that of original sea water. As seen in Fig. 2 the absorbance decreases with the lowering of the pH in sodium acetate buffer solution (reagent B). It is found, however, that two curves do not coincide with each other but intersect at pH value of 5.24. This might imply that under such a pH condition the color development of azomethine H—boron complex occurs independently of the change in ionic strength (salinity) in 28–35‰ range.

In this connection, the absorbance of azomethine H—boron complex was measured for sea waters under the specified pH condition (pH=5.24) as determined above. A series of solutions with various ionic strength (salinity) was prepared by diluting the open ocean water (4.5 ppb B) with distilled-deionized water, that is 0, 20, 40, 60, 80, and 100% sea water which correspond directly to the relative concentration in the solutions. The absorbance-salinity relation at 420 nm of wave length are given in Fig. 3. It is seen from the figure that there exists a linear relation between salinity (=boron content) and absorbance unless the reaction time for color development and the concentration of reagent A change throughout automated procedure. This results reconfirms that the removal of the effect of salinity on absorbance of the complex is possible by fixing the pH condition at 5.24.

Effects of azomethine H content and reaction time on color development are also tested as given in Fig. 3. It is found that about 25% increase in the concentration of azomethine H brings about 35–50% increase in absorbance and four minutes

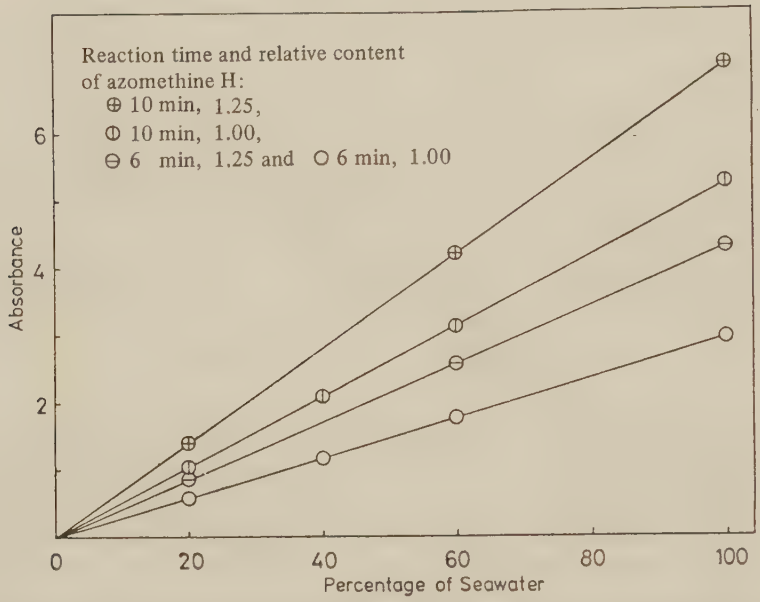

Fig. 3. Relation between absorbance and salinity, involving effect of reaction time and concentration of azomethine H on color development.

increase in reaction time by using a delay coil in flow system also brings about 65–80% increase in absorbance. The effect of concentration of azomethine H and time of reaction on color development are given to be 1–2%/% and 15–20%/min., respectively. These results suggest that above variables should be controled as strictly as possible.

Standard addition method was applied to obtain an absorbance—concentration relation for calibration, by using the stock solution containing 80% of open ocean water. Results are given in Fig. 4. Each curve obtained shows fairly good linear relation, respectively. It is, however, found that there exists the difference in inclination among them, which could be due to a silght variation in the experimental condition in each run in terms of amount and concentration of reagents, flow rate, reaction time, instrumental setting and so far. It should be noted that the values obtained from extrapolating of each curve fairly agree with each other, that is, 3.62 ± 0.01 mg B/1.

The time variation of sensitivity during a consecutive run of several tens samples is given in Table 1. The values of absorbance of column (I) are initially obtained by the duplication of a set of working standards, those of column (II) are obtained 40 minutes later (after 14 samples runs) and those of column (III) are obtained 86 minutes later (after another 22 samples run). Over-all fluctuation in absorbance values measured is estimated to less than ± 0.018 mg B/1 which includes the error produced

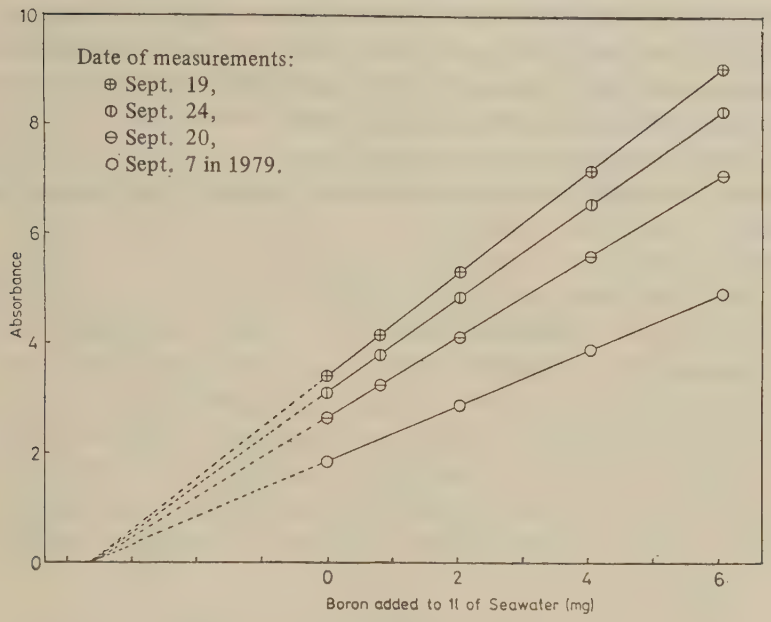

Fig. 4. Relation between absorbance and boron concentration.

Table 1. Test of the method on reproducibility against time.

Working standard		Absorbance (recorder responce)			Average
No.	Conc. (mgB/l)	(I)	(II)	(III)	
1	3.62	449 449	448 447	451 451	449.2±1.6
2	4.43	549 549	551 547	551 551	549.7±1.6
3	5.64	695 698	698 698	700 700	698.2±1.8
Time, (min.)		0	40	86	

by the drift of baseline and slight change in a sensitivity due to decaying of color reagent. When the corrections on change in sensitivity and baseline are performed by introducing a reference standard and boron free washing solution in every 15–20 samples run, the reproducibility of boron measurement in sea water can be lowered to ±0.01 mg B/1.

4. Concluding remark

Usually in manual analysis of boron, it is necessary to stand a sample for at least two hours or so to complete a color development. On the other hand, in the auto-

mated analysis, since the experimental condition such as time for reaction, amount of reagents, flow rate and so far can be strictly controled, much better reproducibility than manual analysis can be obtained even if measurement was done prior to getting maximum color development as demonstrated above.

As far as measurement on board the ship is concerned, the filtration of suspended matters in sea water sample as pretreatment is not necessary. It is secured that there

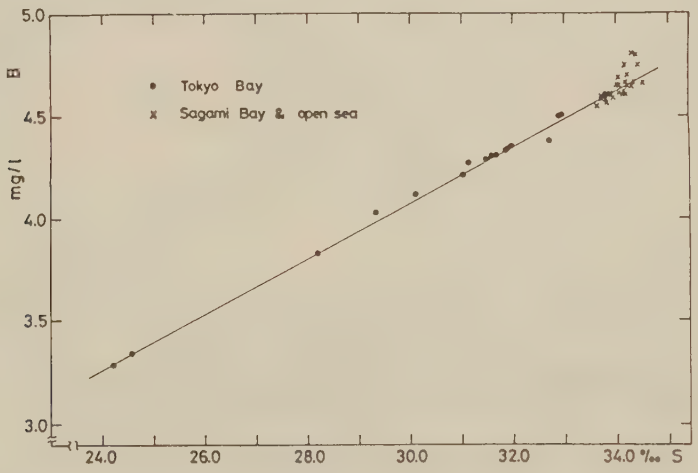

Fig. 5. Relation between boron and salinity in the sea water of Tokyo Bay and adjacent coastal region.

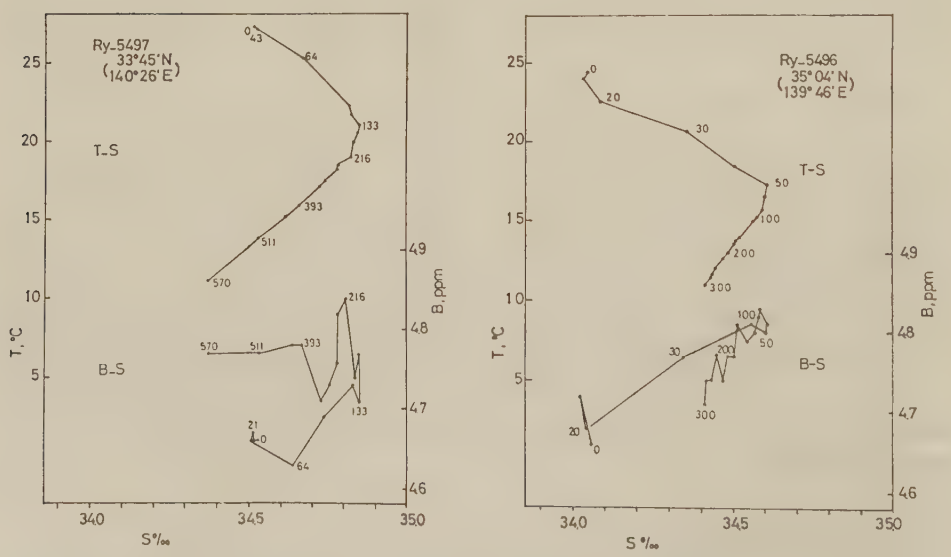

Fig. 6. Boron-salinity and temperature-salinity relations in the open ocean.

is no appreciable difference in boron content between the filtered and unfiltered sea water on board.

It is concluded that an analytical procedures presented above is applicable with reliability enough to determine boron in the sea water with wide range of salinity—coastal to open ocean.

The horizontal and vertical distribution of boron are exemplified as the application of the method to the boron analysis in the sea water in Figs. 5 and 6, respectively.

The boron content in the Tokyo Bay and adjacent coastal regions is found to be ranging from 3.25 to 4.80 ppm which shows a linear relation with salinity. On the other hand, vertical distribution in open ocean shows not so definite correlation with temperature and salinity. The boron—salinity ratio is not constant but varies with depth. It is suggested that the ratio or boron concentration could be used in distinguishing a fine structure of water masses and in tracking ocean currents. A detailed discussion on this matter will be done elsewhere.

The expence for present study was defrayed by the financial aid of the Agency of Science and Technology for the Kuroshio Exploitation Research Program.

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海水中のホウ素の自動分析

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海水中のホウ素の船上分析法として，アゾメチンHを用いた自動分析法の開発を行なった。内湾，沿岸および外洋の海水試料への本法の適用の結果，充分な精度をもってこれらの試料中のホウ素の定量が可能であることが確められた。

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NOTE

Cadmium in marine environment around Japan during 1972–1981

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Studies of the marine environmental pollution of trace metals are potential great importance as well as studies on the chemical and/or biological processes involving trace metals.

It is readily known throughout previous studies that the concentration of cadmium in the marine environment increases rapidly with depth to 1000 m, indicating uptake by organisms at the surface and regeneration from sinking biological debris at deep in water column.

BENDER and GANGER (1976) reported the values of surface (0.05 nmol/kg) and deep (0.30 nmol/kg) for the Sargasso Sea, and KNAUER and MARTIN (1973) gave the values for 1000 m depth near Hawaii (1 nmol/kg) and surface (<0.2 nmol/kg). BOYLE *et al.* (1978) gave the values for temperate Mid-Pacific, east of Japan; surface (0.12 nmol/kg) and 1126 depth (1.08–1.09 nmol/kg) and also for the North Pacific upwelling region in the Bering Sea; surface (0.61 nmol/kg) and deep (0.99–1.16 nmol/kg). BRULAND *et al.* (1978) gave 0.041 nmol/kg for surface and 1.13 nmol/kg at the depth of the nutrient maxima in the northeast Pacific water.

The report presented here describes the time and spacial distribution of cadmium and its vicissitudes in marine environment around Japan, based on the cardium monitoring data reported by the Japan Meteorological Agency (1973–1981).

Station locations were deployed so as to cover a broad range of oceanic conditions in the region involved, as shown in Fig. 1, where the samples for cadmium analysis were taken four times a year. Sea water samples were collected by using Niskin bottles, acidified on board ship by adding HCl immediately after sampling, and stored in acid-leached polyethylene bottles for several months in the laboratory on land. Cadmium in 0.8–5.0 *l* aliquot of sea water sample was extracted into 20–200 ml of dithizone-CCl_4, followed by the back extraction using 10–20 ml of 6N HCl solution, and analyzed by the atomic absorption spectrophotometry. The analytical error in the method is estimated to be within ± 0.05 nmol/kg.

Time series of cadmium data in the seas around Japan are graphically represented in Fig. 2-a and 2-b. Since the values of cadmium concentration fluctuated, the original

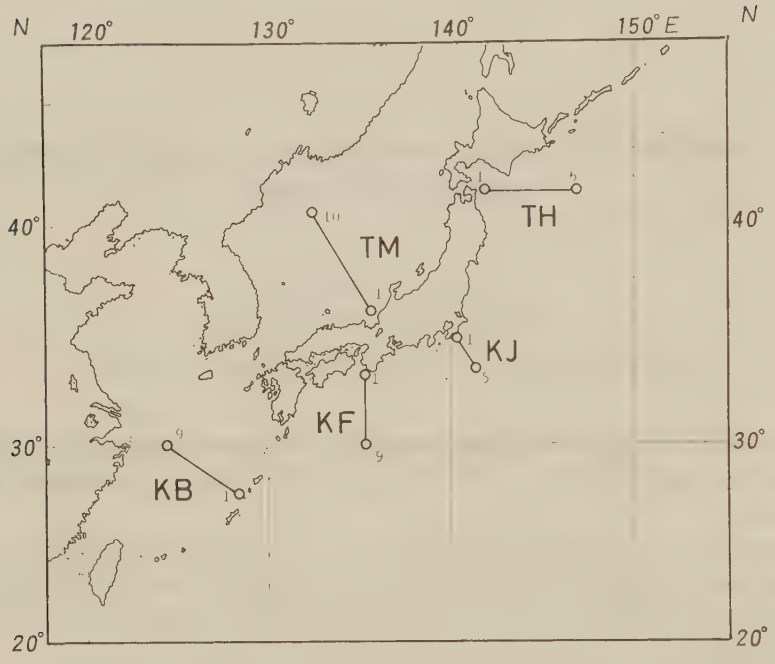


Fig. 1. Observation lines and sampling stations for monitoring background marine pollution.

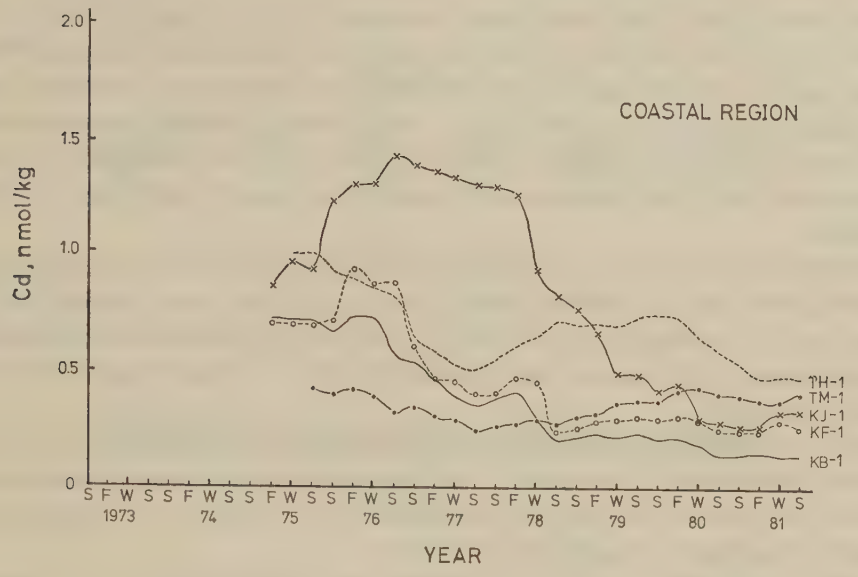
data sequence was smoothed by 10-term moving averages in this case.

The high level of cadmium concentration, reaching upto about 1.5 nmol/kg, is found in the coastal waters along the Kuroshio region in the first half of the period. The concentration level increases in the order of KB-1, KF-1 and KJ-1 toward downstream of the Kuroshio. Then the levels go down rapidly to the range of 0.2–0.4 nmol/kg which is close to values of Pacific surface water given previously. The range of cadmium concentration in the region is found to be factor of around 10.

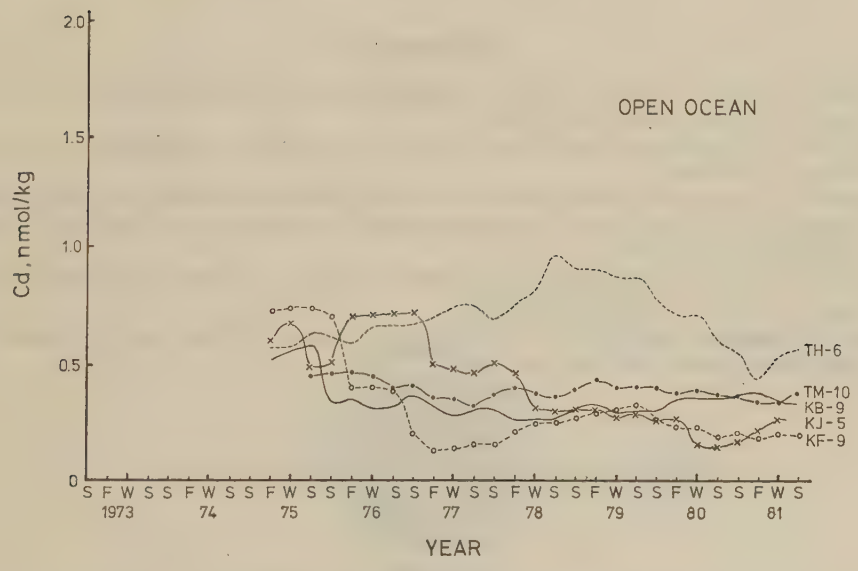
The region of open ocean far out of the Kuroshio (KB-9, KF-9 and KJ-5) shows not so distinctive time variation of cadmium concentration as the coastal region but shows only appreciable increase in cadmium level before 1974–75. The range of cadmium concentration is less than factor of about 2.

As for the Eastern China Sea present level of cadmium concentration is rather higher in the water situated on the continental shelf (KB-9) than that in the coastal region off Ryukyu Islands (KB-1). In the Japan Sea the cadmium concentration varies so slightly against time and that its difference between coastal (TM-1) and offshore (TM-10) regions is so small unlike the Kuroshio region; KF and KJ. The fluctuation range observed is only within ± 0.05 nmol/kg.

The TH lines show quite different patterns in time variation from other four regions. It is seen from Fig. 2-a and 2-b that there exist the fluctuations with relatively wide



a. Coastal region



b. Open ocean

Fig. 2. Time variation of cadmium concentration in the sea adjacent to Japan.

range, factor of 2–3, compared with other four regions and no difference in concentration range between TH-1 and TH-6. Even the lowest value of cadmium concentrations at TH-1 and TH-6 is found to be respectively still the highest of present values obtained in the other regions. The range of cadmium concentration obtained is close

to the values given for the North Pacific upwelling region in Bering Sea (BOYDE *et al.*, 1976). It is safely said that the pattern in the time variation and higher cadmium concentration in the TH region could not reflect the enrichment of cadmium due to environmental pollution but rather higher natural level of cadmium concentration in this region. The wide fluctuation probably results from the interaction of waters in the region such as the Tsugaru warm current, Oyashio and relevant waters involving upwelling.

The cadmium concentration of deep water (500–1000 m depth) of the seas adjacent to Japan shows 0.8–1.0 nmol/kg which is the same as the values obtained for the deeper water in the western North Pacific, and the trend of year-to-year and site-to-site variation found in the surface waters is not reflected on the cadmium concentration in the deep water.

From the time series of cadmium data it can be said that presentday level of cadmium concentration is no uniquely high compared with the values of other marine environment reported previously and could reflect the various level of natural background, not artificial contamination.

Further accumulation of data on cadmium will provide more useful information on the vicissitudes of cadmium in marine environment.

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1972–1981年の日本周辺海洋環境のカドミウム

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海洋バックグラウンド汚染観測業務の一つとして実施されているカドウミムの観測結果を用いて，日本周辺海域でのカドミウム濃度レベルの海域による変化とその時間的な推移を明らかにした。

気象庁

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